

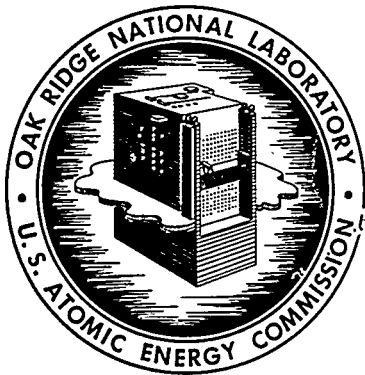
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WASTE TREATMENT AND DISPOSAL
PROGRESS REPORT
FOR APRIL AND MAY 1961



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for the
U.S. ATOMIC ENERGY COMMISSION

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CHEMICAL TECHNOLOGY DIVISION
AND
HEALTH PHYSICS DIVISION

WASTE TREATMENT AND DISPOSAL PROGRESS REPORT
FOR APRIL AND MAY 1961

R. E. Blanco and E. G. Struxness

DATE ISSUED

AUG - 1 1961

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

ABSTRACT

High-Level Waste Calcination. Simulated Purex sulfate-bearing wastes were incorporated into magnesium and calcium phosphate and borophosphate ceramic glasses with densities varying from 2.6 to 2.8 g/cc. The volume of solid product per ton of uranium processed varied from 4.8 to 6.9 gal. The leaching rate of a typical magnesium borophosphate "glass" decreased from 3.2 to 10^{-2} g_{cm}⁻² day⁻¹ at 8 hr exposure to approximately 4.5×10^{-3} at 10 days and 8.4×10^{-5} at 35 days. No detectable ruthenium was volatilized during evaporation-calcination of Purex, Darex, or TBP-25 solutions containing 1.5 M H₃PO₃ to temperatures of 500-900°C. When the initial phosphite concentration was 0.1 M, no ruthenium was volatilized until the temperatures rose above 150°C. Continuous addition of 0.1 M H₃PO₃ to the feed solution followed by final addition of H₃PO₃ to give a product equivalent to 0.4 M H₃PO₃ in the feed resulted in volatilization of 1.4% of the total ruthenium vs 4.9% when the initial feed solution was 0.4 M in phosphite and no further phosphite addition was made. No net off-gas was produced in either case.

Two full-scale tests of the close-coupled pot-calcination process were completed in the 8-in. dia x 84-in.-high pot calcination units fed directly by a continuous 25-liter-capacity still. In the first run, standard sulfate-bearing Purex waste was made 1.2 M in sodium and 0.2 M in magnesium to decrease sulfate volatility and processed at an average rate of 21 liters/hr. Only 0.2% of the sulfate volatilized. However, the cake melted and corrosion was excessive in the pot contrary to expectations from previous small-scale runs with magnesium additive and large-scale runs with calcium additive. The second run with TBP-25 aluminum-bearing waste was completely successful in terms of feed rate, evaporator and pot control, and corrosion. The final product density was 0.56 g/cc.

Low-Level Waste Treatment. The scavenging-ion exchange process was tested in a small pilot plant (60 liters/hr) on ORNL low-level waste to obtain scaleup data. The units in sequence are a flash mixer, flocculator, sludge-blanket clarifier, anthracite filter, polishing filter, and ion exchange column. The ion exchange resin was CS-100, a carboxylic-phenolic resin. Feed clarification was excellent and produced an effluent with 3 ppm turbidity and 8 ppm dissolved hardness as CaCO₃. Decontamination factors were equal to or better than design specifications and confirmed laboratory-scale results, i.e., decontamination factors for strontium and cesium ≥ 1000 for overall waste volume reductions ≥ 3000 , gross β activity 54% of the mpc_w , assuming 100% Sr-90, for 168 hr per week and strontium and cesium 1% or less of the mpc_w 's for a 168-hr week. Design of a 10-gpm pilot plant is complete and completion of construction is scheduled for August 1961.

A dosage of 125 ppm of PO₄[≡], as a supplement to normal lime-soda ash treatment, increased strontium removal from ORNL process waste. The floc produced had better settling character than that produced by primary coagulation with phosphate, and as much strontium was removed as in the most efficient primary phosphate treatment,

and careful pH adjustment was not required. A combination of coagulant aids, 1.0 ppm of Hagan 323, and 2.0 ppm of Hagan 2 greatly improved the settling characteristics of the floc. During a one-week plant test, removals of Sr-89-90 and Cs-137 increased from 79% to 87% and from 85% to 97%, respectively. Second stage treatment of ORNL process waste with sodium-treated vermiculite (grade BO-4) gave distribution coefficients for strontium and cesium >5000 .

Engineering, Economic, and Hazards Evaluation. A comprehensive study has been undertaken to evaluate the economics and hazards associated with alternative methods for ultimate disposal of highly radioactive liquid and solid wastes. The study should define an optimum combination of operations from the many available. A 6-tonne/day plant is assumed, processing 1500 tonnes/year of 10,000 mwd/tonne uranium and 270 tonnes/year of 20,000 mwd/tonne thorium, equivalent to all the fuel from a 15,000 Mw_e nuclear economy ca. 1970.

Interim storage of high-level liquid wastes from such a plant for 0.5 to 30 years was estimated to cost from 2.0×10^{-3} to 9.3×10^{-3} mill/kwh_e for acidic wastes in stainless steel tanks and from 1.5×10^{-3} to 4.7×10^{-3} mill/kwh_e for neutralized wastes in mild steel tanks for optimum combinations of filling time and full time and based on present worth considerations.

A cost study of conversion to solids by pot calcination is in progress. Capital costs were estimated for the calcination plant building as a function of building size, which varies with different combinations of acid and neutralized wastes and with pot diameter; and as a function of shielding wall thickness, which varies with interim liquid storage time before calcination. Processing equipment costs were also estimated, but operating cost estimates, including cost of the disposable calciner vessel, are not yet complete. For seven different types of calcined solids which might be produced from wastes from the assumed 6-tonne/day fuel processing plant, for pot diameters from 6 to 24 in. and for interim liquid storage times from 0.5 to 30 years before calcination, the capital costs for pot calcination varied between 1.2×10^{-3} and 2.8×10^{-3} mill/kwh_e.

Disposal in Deep Wells. Two ORNL drilling crews, with two crews from the Corps of Engineers, have completed 15 test holes in the area of the second fracturing experiment. Partial analysis of the test drilling show that the geologic structure is more complex than anticipated and that folds or faults in the shale have influenced the shape of the grout sheet. Nothing that has been found is unfavorable to the potential use of fracturing disposal but the shape of the grout sheet is not that anticipated from earlier work. A contract has been let for a 3000-ft core hole to determine the possibility of injecting waste into the lower part of the Rome formation.

Disposal in Natural Salt Formations. Wastes have been removed from the large test cavities and shipped to Wichita for disposal. Measurements and photographs of the walls of both cavities will be compared with those taken before the cavities were filled.

Undercutting in the acid waste cavity is below the liquid level in the form of pockets in the wall 4 to 6 in. deep. About 1 ft of recrystallized salt is deposited on the bottom of the cavity. In the neutralized cavity the undercutting is above the liquid level, with a buildup of recrystallized salt at the liquid level, on the walls below the liquid level, and at the sludge-liquid interface.

Measurements of plastic flow around the test cavities in the Carey mine are completed. In the center of the room, the rate of movement prior to startup was 0.0005 in./day; when the power was cut off 400 days later, the rate of movement was 0.0004 in./day. The total floor-to-ceiling movement for the duration of the heating cycle was 0.65 in., about 0.50 in. more than would have occurred normally.

Clinch River Studies. An estimate has been made of fission product activities (Sr-90, Cs-137, Ru-106, and Co-60) in bottom sediments of the Clinch River from CRM 4.7 to CRM 21.6. Eight to ten cores were collected from each of nineteen cross-sections and individually analyzed for gross gamma activity. The computed average gamma activity for each cross-section compares favorably with "Flounder" measurements by the Applied Health Physics Section.

All cores from each cross-section were composited and analyzed for specific nuclides. Except for Ru-106, radiochemical analyses show a maximum specific activity at the mouth of White Oak Creek (CRM 20.8) and another maximum downstream at CRM 11.0. Ru-106 increased from its minimum concentration at CRM 20.8 to a maximum at CRM 8.0.

The specific activity ($\mu\text{c/g}$) in each section was multiplied by the density and cross-sectional area of the silt in the section to give the activity in curies per mile. The total number of curies, obtained by integrating the data from CRM 21.6 to CRM 4.7, was found to be about 145: 98.0 curies of Cs-137, 33.2 curies of Ru-106, 11.6 curies of Co-60, and 1.83 curies of Sr-90.

Fundamental Studies of Minerals. Sorption of strontium by 0.5 g of vermiculite from 0.1 M NaNO_3 solution containing 1.1×10^{-5} M strontium after 24 hr contact was increased from 20% removal by natural vermiculite (pH 6.5) to 45% by vermiculite leached with 1 M NaCl (pH 6.5), to 70% using NaCl-NaOH treatment (pH 9), and to 83% after sodium tetraphenylboron treatment (pH 9).

Sorption of strontium at selected pH's showed an increase of 35% in sorptive capacity at pH 9 compared to pH 4.

Addition of potassium salts increased the sorption of cesium by natural vermiculite from 0.5 M NaNO_3 solution containing 1.7×10^{-7} M cesium by changing the sorption mechanism from "edge fixation" to "interlayer fixation." Potassium additions to levels of 10^{-4} , 10^{-3} , 10^{-2} , and 10^{-1} M resulted in respective cesium K_d 's of 15, 9.5, 925, and 44 ml/g. Lattice collapse, and interlayer fixation, was initiated at

10^{-2} M K^{+} , though complete collapse did not occur until the potassium concentration was increased to 10^{-1} M. The decrease in K_d at 10^{-1} M potassium is caused by increased competition between potassium and cesium for the interlayer fixation sites.

White Oak Creek Basin Study. In Burial Ground No. 4, 31 to ≤ 1 c/m/ml of gross activity has been detected in 8 of 16 observation wells, varying with the sampling period. In several wells the concentration of activity increases as the water table rises, while in others the inverse occurs. The additional water accompanying a rise in water level may cause increased leaching of waste but may also act as a diluent of the waste solution. Interpretation of these data is complicated by the heterogeneity of the waste and the lack of detailed information on burial operations. Increased amounts of Na^{+} , Cl^{-} , NO_3^{-} , and $SO_4^{=}$ are also present in contaminated wells. The first month of stream monitoring below the northeast portion of the drainage basin, subject to air-borne contamination and drainage from Burial Ground No. 3, showed that 7.6 mc of Sr-89-90, 2.7 mc of rare earths, 0.53 mc of Cs-137, and 0.013 mc of Zr-Nb-95 was contributed to White Oak Creek.

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1.0 INTRODUCTION

This report is the first of a series of bimonthly reports on progress in the ORNL development program, the objective of which is to develop and demonstrate on a pilot plant scale integrated processes for treatment and ultimate disposal of radioactive wastes resulting from reactor operations and reactor fuel processing in the forthcoming nuclear power industry. The wastes of concern include those of high, intermediate, and low levels of radioactivity in liquid, solid, or gaseous states.

Principal current emphasis is on high- and low-level liquid wastes. Under the integrated plan, low-level wastes, consisting of very dilute salt solutions, such as cooling water and canal water, would be treated by scavenging and ion exchange processes to remove radioactive constituents and the water discharged to the environment. The retained waste solids or slurries would be combined with the high-level wastes. Alternatively, the retained solids or the untreated waste could be discharged to the environment in deep geologic formations. The high-level wastes would be stored at their sites of origin for economic periods to allow for radioactive decay and artificial cooling. Interim storage and cooling, which can be accomplished safely in conventional storage tanks, greatly simplifies the problems of subsequent handling and should decrease the overall cost of waste management. Studies (1) have shown that the cost of permanent tank storage may not be excessive, but its safety is questionable.

Alternative methods to tank storage for ultimate treatment and disposal are being investigated to find safer and possibly cheaper methods. One approach is to convert the liquids to solids by high temperature "pot" calcination or fixation in the final storage container (pot) itself and store it in a permanently dry environment such as a salt mine. This is undoubtedly the safest method since complete control of radioactivity can be assured within present technology during treatment, shipping, and storage. Another approach is to dispose of the liquid directly into sealed or vented salt cavities. Research and development work is planned to determine the relative feasibility, safety, and economics of these methods, although the major effort will be placed on conversion to solids and final storage as solids.

Tank storage or high-temperature calcination of intermediate-level wastes may be unattractive because of their large volumes. Consequently, other disposal methods will be studied. One method, e.g., addition of solidifying agents prior to direct disposal into impermeable shale by hydrofracturing, is under investigation at present. Particular attention is given to the engineering design and construction of an experimental fracturing plant to dispose of ORNL intermediate-level wastes by this method if proved feasible.

Environmental research on the Clinch River, motivated by the need for safe and realistic permissible limits of waste releases, is included within the scope of this program. The objective is to obtain a detailed characterization of fission product

distribution, transport, and accumulation in the physical, chemical, and biological segments of this environment.

2.0 HIGH-LEVEL WASTE CALCINATION

The pot calcination process for converting high-level wastes to solids is being studied on both a laboratory and engineering scale to provide design information for construction of a pilot plant. Development work has been with synthetic Purex, Darex, and TBP-25 wastes containing millicurie amounts of ruthenium but has not been demonstrated on actual high-activity-level wastes.

Purex waste was used to demonstrate the general flowsheet shown in Fig. 2.1. The waste is fed into an evaporator where it is combined with concentrated nitric acid and dilute nitric acid or water recycled from the pot calciner and rectifier, respectively, to maintain the acid concentration below 6 M. to minimize ruthenium volatility. Evaporation is either batch or continuous but a catch tank would be used between the evaporator and calciner for batch operations. This flowsheet differs from that shown previously (1) in that the calciner off-gases are recycled through the evaporator and water is added to the evaporator continuously. The evaporator bottoms go to an electrically heated pot, at essentially their initial concentration, where they are evaporated to dryness and calcined to 900°C. Additives may be added prior to calcination to reduce sulfate and fission product volatility or produce a melt (glass) in the pot after calcination. The stainless steel pot would be welded shut and serve both as the shipping and ultimate containment vessel. About 90% of the nitrogen oxides in the calciner off-gas are absorbed in the condenser and the remainder in the evaporator-scrubber or the rectifier. About 1 ft³ of noncondensable gas per gallon of feed is produced, thus minimizing the size of the final absolute filter. Calcination rates and heat dissipation rates in ultimate storage media are satisfactory (1,2).

2.1 Evaporation Calcination

2.1.1 Laboratory-scale Studies (W. E. Clark and H. W. Godbee)

Bench-scale experiments were performed in previously described equipment (Fig. 6.2 in ref. 1) consisting of an 18- x 4-in.-dia stainless steel pot in a 9-kw furnace, a downdraft condenser, packed absorber column, polyethylene expansion bag (to measure net noncondensable gas volume), and gas recirculation pump. The objective of the experiments was to minimize ruthenium volatility by adding NO gas to the calciner and to minimize sulfate volatility by adding 10% stoichiometric excess of sodium and magnesium to the waste. Calcium, rather than magnesium had been used in previous experiments but a CaSO₄ precipitate formed in the feed. Synthetic 40 gal/ton of uranium processed Purex waste to which 1.2 and 0.2 mole/liter of NaOH and MgO, respectively, had been added, were evaporated at an initial boiloff rate of 100 ml/min and calcined to 900°C (Table 2.1). The final

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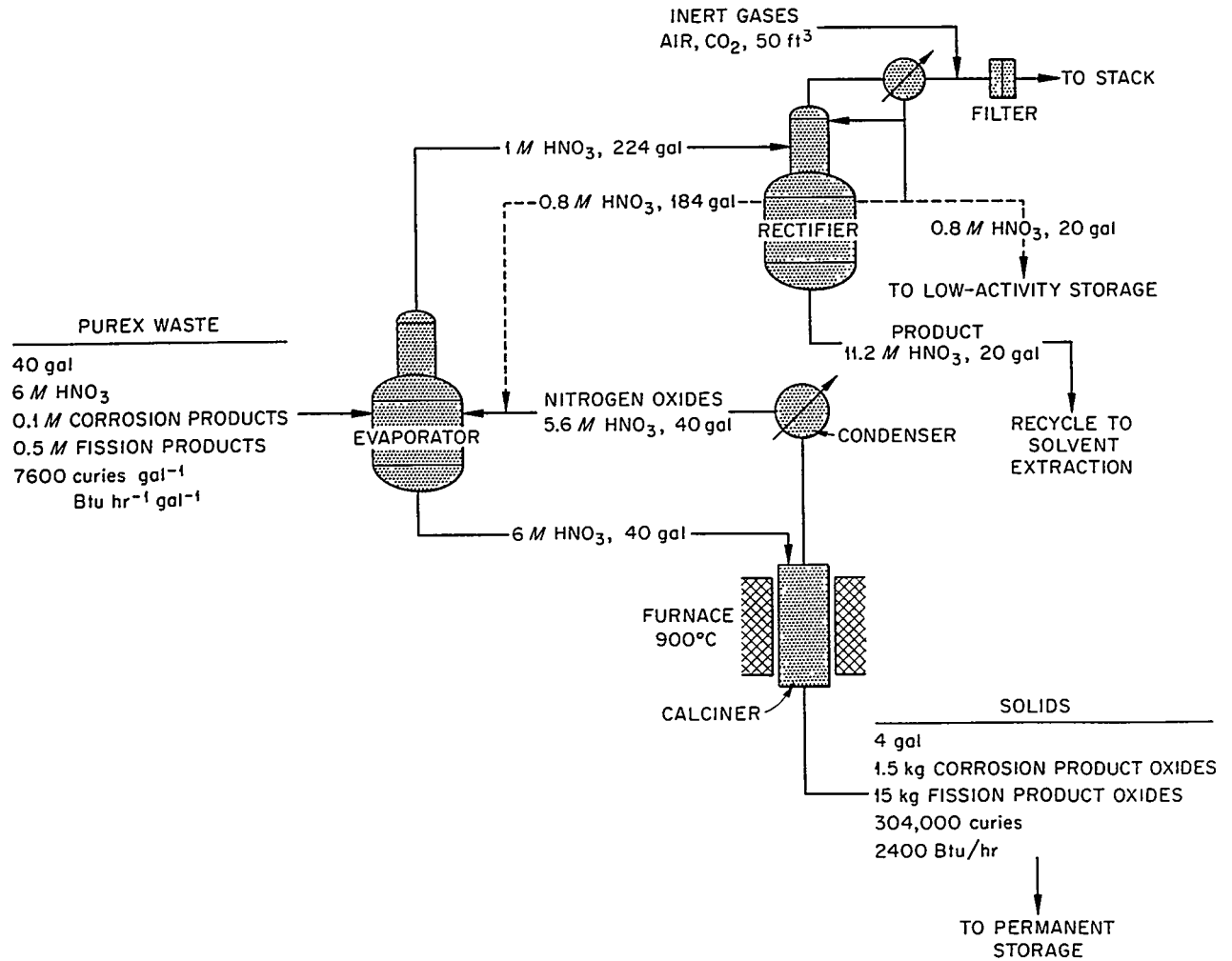


Fig. 2.1. Flowsheet for Converting Purex Waste to Solid for Storage.

Table 2.1 Bench-scale Continuous Evaporation and Pot Calcination of Purex Waste to 900°C

Initial waste compositions: 6.1 M NO_3^- , 5.6 M H^+ , 1.0 M SO_4^{--} , 0.6 M Na^+ , 0.5 M Fe^{++} , 0.1 M Al^{3+} , 0.01 M Cr^{3+} , 0.01 M Ni^{++} , 0.002 M Ru; equivalent to 40 gal/ton U processed

Calciner dimensions: 18 in. high, 4 in. dia

Expt. No.	Additive (moles/liter)	Nitric Oxide Sweep Rate (moles/liter)	Volume (gal/ton U)	Residue Density (g/cc)	Description of Residue	% of Original	
						In Residue, NO_3^-	In Condensate SO_4^{--} Ru
1	1.2 NaOH 0.2 MgO	0.40	5.7	1.32	Hard brown solid calc. porosity 58%	0.18	0.28 31.8*
2	1.2 NaOH 0.2 MgO	0.39	4.0	1.86	Hard brown solid calc. porosity 41%	0.18	0.51 45.8*
3	1.2 NaOH 0.2 MgO	0.36	4.5	1.66	Hard brown solid calc. porosity 47%	0.21	0.70 19.5**
4	1.2 NaOH 0.2 MgO	0.43	4.2	1.78	Hard brown solid calc. porosity 43%	0.25	0.56 17.6**

* NO introduced into vapor space of calciner pot.

** NO introduced into liquid feed entering calciner pot.

volume was 5.7 gal/ton U with a bulk density of 1.32 g/cc, equivalent to a calculated porosity of 58%. Nitric oxide addition was regulated to 0.40 mole per liter of waste to hold the system at atmospheric pressure. In three similar experiments with initial boiloff rates of 125 ml/min, the volumes were decreased to 4.0, 4.5, and 4.2 gal waste/ton U with NO consumption of 0.39, 0.36, and 0.43 mole per liter of waste, respectively. The smaller final volumes were attributed to the higher boiloff rates as in previous experiments with NO added to the system during evaporation-calcination, the net off-gas production was nil. Analyses for stable ruthenium showed 31.8, 45.8, 19.5, and 17.6%, respectively, of the original ruthenium in the condensate (Table 2.1). The two higher values were obtained when NO was introduced into the vapor space of the calciner, while the two lower values were obtained when NO was introduced into the liquid feed line to the calciner. Sulfate in the condensate varied from 0.28-0.70% of the original sulfate in the feed and appears to be caused mainly by entrainment.

2.1.2 Engineering Scale Studies (J. C. Suddath, C. W. Hancher)

Calcination studies in the engineering-scale pot calciner have been made with simulated Purex, Darex, and TBP-25 aluminum-containing waste with and without additives to control sulfate volatility and to give lower fusion temperatures. Nine calcination tests have been made under a variety of conditions, including the use of a close-coupled evaporator in the last three tests (Table 2.2).

Successful operation of the calciner with Purex waste was demonstrated when calcium was added (0.7 M) to suppress sulfate volatility (3a), the only difficulty being feeding of a slurry of CaSO_4 to the calciner. A dense cake with a bulk density of 55% of theoretical was obtained which filled 95% of the pot. The solidity and uniformity of the cake along the pot walls may be seen in Fig. 2.2 but the center has been somewhat disrupted by the vigorous handling required to split the pot. The final volume was about 6 gal per ton of uranium processed. When the Purex waste contained no additive (run 36), considerable segregation and probably melting occurred. When the waste contained 1.2 M sodium and 0.2 M magnesium as additives (run 37) both severe corrosion and segregation occurred unexpectedly, contrary to the results of previous small-scale (4- x 12-in. pot) runs (see Sect. 2.1.1).

Excess sodium sulfate was added to Purex waste in runs 32 and 33 to decrease fusion temperature. A fused cake (density 2.5 g/cc) was obtained but a large and sudden amount of gas evolution during the later stages of the test caused the molten contents of the pot to be carried up into the off-gas system. Consequently, the use of melt conditions of this type where bridging can occur is not recommended.

With Darex and TBP-25 wastes there were no operating difficulties. The close-coupled evaporator was used for recycle of TBP-25 waste. Operation was satisfactory but deposition of mercury compounds in the off-gas lines was a problem.

Table 2.2 Engineering Scale Evaporation and Pot Calcination of Waste to 900°C

Run No.	Waste Type	Avg. Feed Rate (l/hr)	Calcliner Size	Solid Bulk Density (g/cc)	Additive	Stoichiometric Ratio in Feed $\text{SO}_4^{2-}/\text{Na}^+ + \text{Ca}^{++}$	Sulfate in Condensate (% of Feed)	Nitrate in Cake (ppm)
30	Purex	16	6" ϕ x 84"	1.5	0.6 M NaOH 0.6 M CaO	1.0*	5.0 (0.05 M)	300
31	"	22	8" ϕ x 84"	1.2	0.6 M NaOH 0.62 M CaO	1.25**	12.0 (0.12 M)	60
32	"	24	"	2.5	1.0 M Na_2SO_4 0.5 M NaOH	1.11	3.0 (0.03 M)	5000
33	"	21	"	2.5	1.0 M Na_2SO_4 0.5 M NaOH	1.11	3.0 (0.03 M)	500
34	Darex (1)	24	"	1.1	None	---	---	300
35	TBP-25 (1)	30	"	0.83	None	---	---	60
36	Purex	20	8" ϕ x 90"	1.2	None	3.34	Not analyzed	Not analyzed
37	Purex	20	"	1.3	1.2 M NaOH 0.2 M MgO	0.91	0.2 (0.002 M)	Not analyzed
38	TBP-25	27	"	0.56	None	---	---	4000

* 1.1 M SO_4^{2-} in Feed.

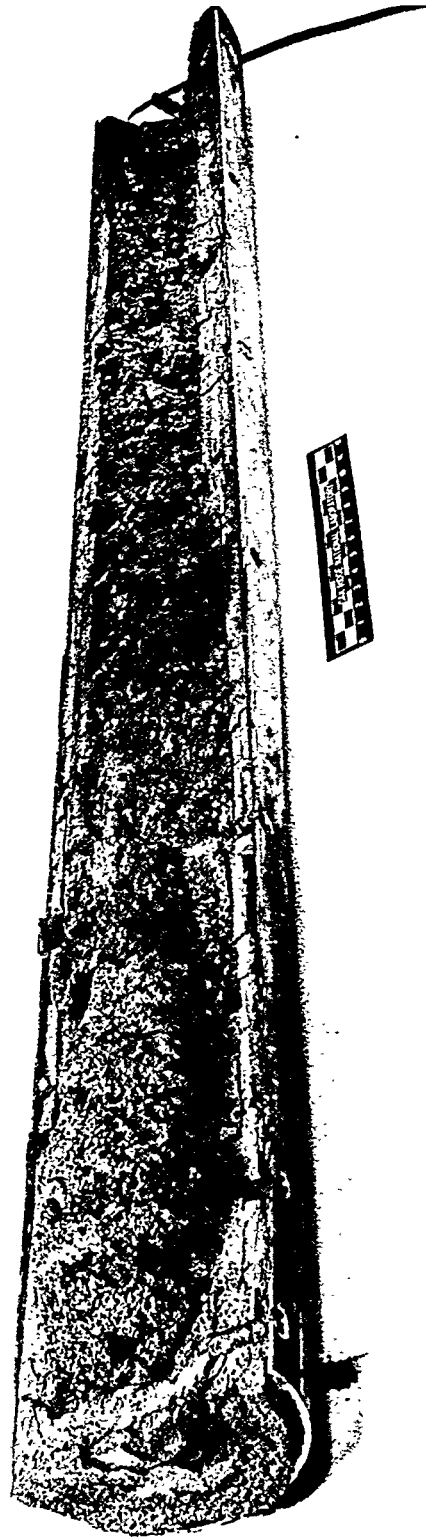
** 1.5 M SO_4^{2-} in Feed.

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(a) PUREX CAKE WITHOUT ADDITIVE

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(b) PUREX CAKE WITH CALCIUM ADDITIVE

Fig. 2.2. Comparison of Calciner Products Showing (a) Segregation and (b) Non-Segregation.

Evaporator-Calciner Test R-37. The purpose of this test was to demonstrate the operability and control of a close-coupled waste evaporator and calciner, previously described (3b). The evaporator used had an operating capacity of 22 liters. The calciner pot was 8-in.-dia by 94-in. high with an operating capacity of about 60 liters. The feed was simulated Purex (40 gal/ton of U) plus 1.2 M sodium and 0.2 M magnesium added to decrease sulfate volatility (Table 2.2). The additional sodium was added as Na_2SO_4 and the magnesium as 0.1 M MgSO_4 and 0.1 M as MgO , this being the only sulfate in feed.

The feed rates varied from 70 to 4 liters/hr, with an average rate of 21.0 liters/hr (Table 2.3). The water addition rate was 172 to 3 liters/hr. The water is added to remove the nitric acid from the evaporator by steam stripping. The evaporator acidity is held to 6 M or less to decrease ruthenium volatility, but no ruthenium was used in this test. The water/feed ratio was 0.05 to 5.80, with an average of 2.4. The water concentration of the evaporator acid was controlled by the evaporator temperature and water addition. The evaporator temperature set point was 113°C , which was predetermined to be approximately 6 M HNO_3 at -0.5 psig and an iron concentration of 25-30 g/liter.

Table 2.3 System Balances and Results for Test R-37

<u>Nitrate Balance</u>		<u>Feed Rate</u>
Input	2469 g moles	404 liter/19 hr (21.0 liters/hr)
Recovery		
Condensate	1776 g moles (72%)	<u>Water Rate</u>
Solid	Remainder	983 liters of water; water/feed ratio = $983/404 = 2.4$
<u>Sulfate Balance</u>		<u>Calcined Solids</u>
Input	390 g moles	78 kg solids/68 liters (1.15 g/cc bulk density)
Recovery		
Condensate	5.0 g moles (0.75%)	
Solid	360 g moles (92.0%)	
<u>Off-Gas</u>		
831 ft ³ total		
440 ft ³ leakage and gas purge (20 ft ³ /hr,		
25% and 75%)		
391 ft ³ noncondensable		
$391/404 = 0.97 \text{ ft}^3/\text{liter of system feed}$		

Calcliner Pot Corrosion. In all previous pot calcination tests corrosion has not been serious. However, in test R-37 a number of holes (5 to 8) about 2 in. dia corroded through the calciner pot 60 to 65 in. from the bottom of the pot. There was also local overheating in this area of the calciner pot from furnace section 2 (Fig. 2.3).

There are five thermocouples per furnace section: (A) center of pot, recording; (B) inside, 1 in. from wall of pot, recording; (C) outside of pot, recording; (C) outside of pot, controlling; (D) in furnace section, controlling.

The power of the furnaces is controlled by a thermocouple attached to the outside of the calciner pot at a set point of 900°C. The thermocouples in the furnace prevent heating above 1200°C. After 17 hr operation all the thermocouples appeared to be operating satisfactorily. Apparently thermocouple (58-in.-C) to the Wheelco control for furnace section 2 was destroyed by corrosion and reported a low temperature, causing furnace section 2 to overheat after the pot had corroded through. The pot was 100-mil 304L stainless steel. The thickness at the elevation around the holes was decreased to about 25 mils (Fig. 2.4).

One explanation may be that at 900°C MgSO_4 decomposed, freeing SO_3 , which mixed with nitric acid available at the corroded zone. The corroded zone was approximately the operating liquid level. In R-36, which contained no Mg or Na and SO_3 and H_2SO_4 were vaporized as a result, the ends of the liquid level probes and feed lines were severely corroded but the wall was not attacked. In R-37 the feed and level lines were not corroded.

Calcined Solid. The calcined solids had a bulk density of 1.3 g/cc (Table 2.2), based on total weight of solids and total volume to the top of the solids. When the calciner pot was slit from end to end and half of the metal shell removed, it was noted that the midsection of the calciner was empty except for a thin outer film 1/4 to 1/2 in. thick. The bottom appeared to have melted and the top had not been calcined. The solid was red-yellow and had an odor of sulfur.

Evaporator-Calcliner Test (R-38). The close-coupled evaporator-calcliner was operated and controlled as an integrated unit with TBP-25 aluminum waste as feed, simulating the sampled composition of tank WM-182 at the Idaho Chemical Processing Plant. Nonradioactive ruthenium was added to determine the ruthenium volatility during the evaporation-calcination operation. The average feed rate was 27.6 liters/hr (Table 2.4). Only 89% of the nitrate was accounted for, and ruthenium and mercury balances were 57 and 42%, respectively. The unaccounted for ruthenium and mercury probably deposited in the off-gas system. The mercury was concentrated by a factor of 4 in the evaporator during the standby period.

Control of the calciner and evaporator was satisfactory for the complete test except for foaming. During one period the evaporator foamed over the top and some 40 liters of feed was lost to the condensate tank.

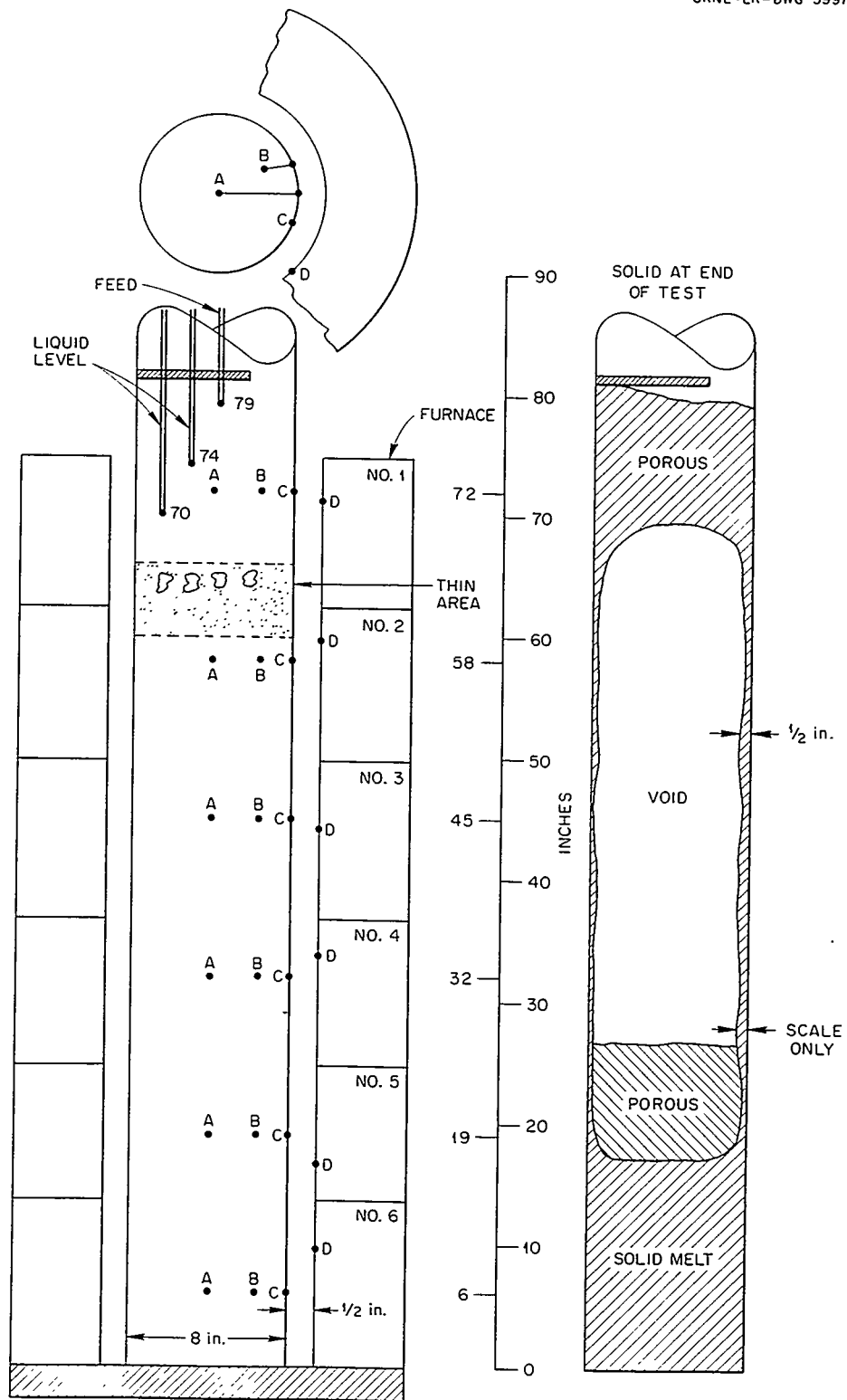


Fig. 2.3. Calciner Pot.

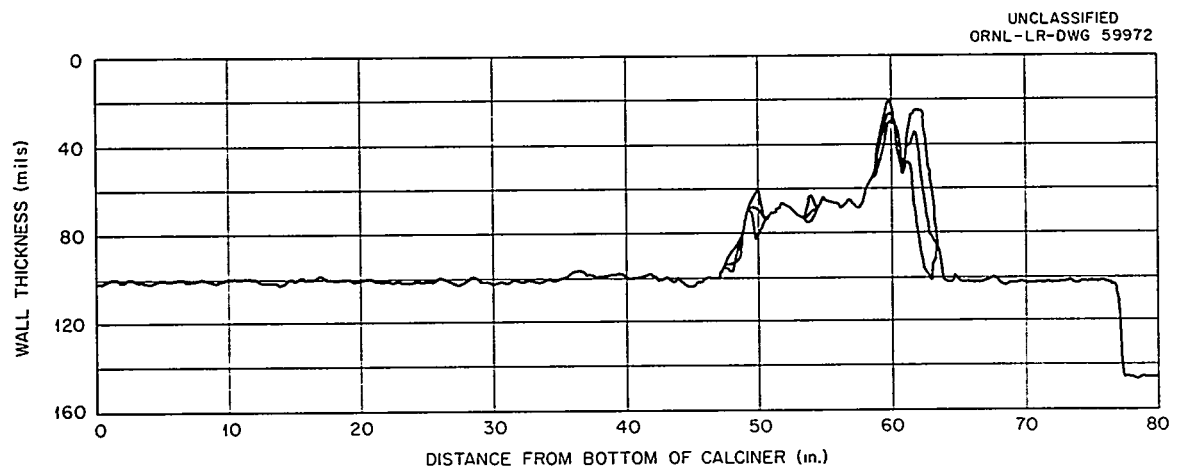


Fig. 2.4. Thickness of Calciner Pots After Testing.

Table 2.4 System Balances and Results for Test R-38

<u>Nitrate Balance</u>			<u>Off-gas</u>
Input	2917 g moles		1260 ft ³ total
Recovery			1152 ft ³ leakage and purge
Condensate	2581 g moles	(88.5%)	108 ft ³ noncondensable (74 ft ³ oxygen)
Solid	3 g moles	(0.1%)	
Off-gas	6 g moles	(0.2%)	108/442 = 0.245 ft ³ /liter of system feed
		<u>88.8%</u>	
<u>Ruthenium Balance</u>			<u>Average Feed Rate</u>
Input	66.5 g moles		442/16 hr = 27.6 liter/hr
Recovery			
Condensate	8.8 g moles	(13.3%)	<u>Water Feed Rate</u>
Solid	28.5 g moles	(43.0%)	1457 liters of water, water/feed ratio = 3.3
Evaporation	0.8 g moles	(1.1%)	
		<u>57.4%</u>	
<u>Mercury Balance</u>			<u>Calcined Solids</u>
Input	2250 g moles		38 kg solid/68 liters = 0.56 g/cc bulk density
Recovery			
Condensate	17 g moles	(0.7%)	
Solid	89 g moles	(3.9%)	
Evaporation	840 g moles	(37.0%)	
		<u>41.6%</u>	

2.2 Fixation in Glasses (W. E. Clark, H. W. Godbee)

An ideal end product of high-level waste disposal is a solid "glass" representing maximum volume reduction and mechanical strength, high thermal conductivity, and high insolubility in natural environmental water. The nearest practical approach to such a material is probably a homogeneous microcrystalline insoluble solid with a vitrified surface to decrease the leachable area. Fixation in an insoluble glass is not considered an essential feature of the waste calcination program since the wastes are to be stored in a dry environment, such as a salt mine. However, the above advantages plus the additional safety achieved during shipment to the ultimate disposal site may warrant the extra cost of fixation.

2.2.1 Borate and Phosphate Glasses

The addition of fluxing agents such as borate, phosphate, or phosphite prior to calcination produces a fluid melt and, on cooling, a dense glass with a low surface-to-volume ratio, a high thermal conductivity, and low leaching rate. The nature and amount of

fluxing agent must be chosen to optimize these properties as well as minimize fission product and sulfate volatility. The high-sulfate Purex waste (Table 2.5) is particularly difficult to process according to these criteria because of the difficulty in retaining sulfate in the solid and because the sulfate tends to impart solubility to the solid product. Past work (4-6) has shown that the sulfate can be retained by the addition of chemically equivalent amounts of sodium, calcium, and/or magnesium. If excess sodium is present some sodium and some fission product cesium will be volatilized. In order to prevent volatility of sulfate on the one hand and of sodium and cesium on the other it is necessary that the chemical equivalent ratios $(\text{Na} + \text{Ca} + \text{Mg})/\text{SO}_4$ and SO_4/Na both be 1 or greater.

In an operating plant where waste analyses may be inaccurate, 10% excess calcium or magnesium would be added to ensure excess metal to avoid sulfate volatility. Even with these restrictions some sulfate may be volatilized from magnesium melts above 900°C due to thermal decomposition of MgSO_4 . These ratios are further modified by the addition of other nonvolatile anions such as phosphate and borate. If the sulfate plus fluxing agent anion equivalents exceeds the metal equivalents, sulfate will volatilize at $700\text{--}900^\circ\text{C}$. Initial results show that borate is equivalent to part of the sulfate in the first ratio given above if the anion equivalents are calculated as metaborate, BO_2^- . The corresponding relation for phosphate has not been clearly defined. If the equivalents of phosphates are calculated as metaphosphate, PO_3^- , part of the sulfate is volatilized in some cases. If the phosphate is calculated as pyrophosphate, $\text{P}_2\text{O}_7^{4-}$, no sulfate volatilizes.

A series of solid products was prepared with borate and phosphate fluxing agents which fulfill to a reasonable degree the above criteria (Table 2.6). Densities were in the range 2.6 to 2.8 g/cc and between 5.2 to 6.9 gal of final solids represented 1 ton of processed uranium (Table 2.6). Solid leach (dissolution) rates (melt 4, Table 2.6) over a 40-day period in distilled water, with Cs-137 tracer, were $10^{-3} \text{ g cm}^{-2} \text{ day}^{-1}$ the first day and dropped rapidly to the limit of detectability, $10^{-5} \text{ g cm}^{-2} \text{ day}^{-1}$ by the thirtieth day. One of the more satisfactory solid products contained 21.5, 29, 6.4, and 8.7 wt %, respectively, of SO_3 , P_2O_5 , B_2O_3 , and MgO (melt 3, Table 2.6, Figs. 2.5 and 2.6).

Another series of glasses was produced from Purex waste using only phosphate as the fluxing agent and sodium and magnesium or calcium to prevent sulfate volatility (Table 2.7). Densities for these "glasses" ranged from 2.7 to 2.8 g/cc, and between 4.8 and 5.7 gal of solid represented one ton of uranium processed. One of the better products contained 23.7, 31.9, and 9.5 wt %, respectively, of SO_3 , P_2O_5 , and MgO and had a density of 2.7 g/cc (melt 7, Table 2.7). About 5 gal of this glass would contain the waste oxides from 1 ton of reprocessed uranium.

A metaborate-metaphosphate glass, which softened at approximately 900°C , was produced from TBP-25 waste (Table 2.5) by adding 1.52, 0.13, and 1.58 moles, respectively, of H_3PO_3 , borax, and NaOH to 1 liter of the waste. A glassy product

Table 2.5 Composition of Simulated High-activity Wastes

Component (moles/liter)	Purex	TBP-25
Al^{3+}	0.1	1.6
Fe^{3+}	0.5	0.002
Cr^{++}	0.01	
Hg^{++}		0.01
Ni^{++}	0.01	
NH_4^+		0.07
H^+	5.6	0.5
Na^+	0.6	
Ru	0.002	
NO_3^-	6.1	5.35
$\text{SO}_4^{=}$	1.0	0.026

was produced. Thus far only preliminary experiments have been carried out with TBP-25 glass formation. Additional studies are needed to define the volatility of mercury and ammonia. Other difficulties arise from the high viscosity of these melts and their tendency to puff and swell before melting.

2.2.2 Leaching Studies

Leach tests in distilled water were made on a metaborate-metaphosphate glass containing Purex waste oxides and sulfates. The glass was made from 500 ml of simulated 1WW Purex containing 1.52, 0.80, 0.26, and 1.84 moles/liter of waste, respectively, of H_3PO_3 , MgO , borax, and NaOH . This mixture was spiked with mixed fission products. The leach rate for this glass decreased from an initial rate of $3.2 \times 10^{-2} \text{ g cm}^{-2} \text{ day}^{-1}$ to $6.6 \times 10^{-5} \text{ g cm}^{-2} \text{ day}^{-1}$ at the end of 37 days.

The radioactive glass sample was leached in a polyethylene cell containing 500 ml of distilled water, which was circulated through the system at 100 ml/min (Fig. 2.7). One-milliliter samples were taken every day, and more water was added to make up for losses due to evaporation and sampling. The water was completely renewed each week with fresh distilled water. The leaching rate is shown in Fig. 2.8.

2.6 Metaborate-Metaphosphate "Glasses" Incorporating Purex Waste Oxides

Purex waste composition (M): 6.1 NO_3^- , 5.6 H^+ , 1.0 SO_4^{2-} , 0.6 Na^+ , 0.5 Fe^{3+} , 0.1 Al^{3+} , 0.01 Cr^{++} , 0.01 Ni^{++} , and 0.002 Ru

Melt	1	2	3	4	5	6	7	8	9	10	11
Additives (moles/liter Purex)											
H_3PO_3	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52
MgO	0.80	0.80	0.80	0.80	0.80	0.80	0.20	0.20	0.60	1.20	-
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.086	0.130	0.172	0.258	0.344	0.516	0.086	0.172	0.172	0.172	0.129
NaOH	1.49	1.578	1.67	1.837	2.01	2.36	2.696	2.872	2.072	0.872	1.578
Ca(OH)_2	-	-	-	-	-	-	-	-	-	-	0.80
Composition of Melt (wt % theoretical oxides)											
Fe_2O_3	11.4	11.1	10.7	10.1	9.6	8.6	11.0	10.4	10.6	11.0	10.7
Cr_2O_3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
NiO	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Al_2O_3	1.5	1.4	1.4	1.3	1.2	1.1	1.4	1.3	1.4	1.4	1.4
RuO_3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Na_2O	20.1	20.9	21.8	23.2	24.5	26.7	29.6	30.7	24.8	15.5	20.2
SO_2	22.9	22.2	21.5	20.3	19.2	17.3	22.1	20.8	21.3	22.0	21.5
P_2O_5	30.9	30.0	29.0	27.4	25.9	23.3	29.8	28.1	28.7	29.7	28.9
B_2O_3	3.4	5.0	6.4	9.1	11.5	15.6	3.3	6.2	6.4	6.6	4.8
MgO	9.2	8.9	8.7	8.2	7.7	7.0	4.2	2.1	6.4	13.3	-
CaO	99.9	100.0	100.0	100.1	100.1	100.1	99.9	100.0	100.1	100.0	12.0
Na to P mole ratio	1.49	1.60	1.72	1.94	2.17	2.63	2.28	2.51	1.98	1.19	100.0
Softening Point (Approximate, °C)	850	850	840	850	850	875	850	850	850	875	950
Density (Measured, g/ml)	2.70	2.70	2.70	2.67	2.69	2.70	2.74	2.78	2.73	2.63	2.74
Density (Theoretical, * g/ml)	2.72	2.70	2.68	2.64	2.62	2.56	2.62	2.58	2.65	2.73	2.61
Waste Oxides in Glass* (wt %)	41.6	40.3	39.1	36.9	34.9	31.4	40.1	37.8	38.6	40.0	39.0
Volume (cal Glass/ton U)	5.2	5.3	5.5	5.9	6.2	6.9	5.3	5.5	5.5	5.5	5.4
Appearance	Bluish green, glassy	Green, very glassy	Green, very glassy	Brown, glassy, segregated	Brown, some glassy portions	Brown with segregation, mostly crystalline	Somewhat glassy, segregation of green and white	Light grey, glassy	Brownish green, some glassy portions	Grey-green, micro-crystalline	Grey-glassy, slight segregation

* Calculated.

2.7 Metaphosphate "Glasses" Incorporating Purex Wastes Oxides

Purex waste composition (M): 6.1 NO_3^- , 5.6 H^+ , 1.0 SO_4^{2-} , 0.6 Na^+ , 0.5 Fe^{3+} , 0.1 Al^{3+} , 0.01 Cr^{++} , 0.01 Ni^{++} , and 0.002 Ru

Melt	1	2	3	4	5	6	7	8	9	10
Additives (moles/liter Purex)										
H ₂ PO ₃	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52	1.52
MgO	0.40	0.40	0.40	0.40	0.40	0.80	0.80	0.80	1.20	-
NaOH	2.12	2.50	2.88	3.26	3.64	1.32	1.70	2.08	2.04	2.12
Ca(OH) ₂	-	-	-	-	-	-	-	-	-	0.399
Composition of melt (wt % theoretical oxides)										
Fe ₂ O ₃	11.9	11.5	11.1	10.8	10.4	12.2	11.8	11.4	10.9	11.7
Cr ₂ O ₃	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
NiO	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Al ₂ O ₃	1.5	1.5	1.4	1.4	1.3	1.6	1.5	1.5	1.4	1.5
RuO ₂	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Na ₂ O	25.1	27.7	30.1	32.3	34.4	18.2	21.1	23.7	22.4	24.7
SO ₃	23.9	23.1	22.3	21.6	20.9	24.5	23.7	22.9	21.9	23.5
P ₂ O ₅	32.2	31.1	30.1	29.1	28.2	33.1	31.9	30.8	29.6	31.6
MgO	4.8	4.7	4.5	4.4	4.2	9.9	9.5	9.2	13.3	-
CaO	-	-	-	-	-	-	-	-	-	6.6
Na to P mole ratio	99.9	100.1	100.0	100.1	99.9	100.0	100.0	100.0	100.0	100.1
Softening Point (Approximate, °C)	1.39	1.64	1.89	2.14	2.39	0.868	1.12	1.37	1.34	1.39
Density (Measured, g/ml)	830	850	850	950	875	875	850	850	975	900
Density (Theoretical, * g/ml)	2.70	2.70	2.74	2.67	2.70	2.70	2.70	2.70	2.70	2.78
Waste Oxides in Glass* (wt %)	2.69	2.68	2.66	2.65	2.64	2.75	2.75	2.74	2.78	2.64
Volume (Gal Glass/ton U)	43.4	41.9	40.6	39.3	38.0	44.5	43.0	41.6	39.9	42.6
Appearance	5.0	5.1	5.2	5.6	5.7	4.84	5.0	5.2	5.4	4.9
	grey- glassy	green micro- crystal- line	light grey- micro- crystal- line	light grey, micro- crystal- line	purplish black glassy	dark green, glassy	green, very glassy	green, very glassy	grey- green, micro- crystal- line	green, glassy

* Calculated.

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1.52 moles H_3PO_3
0.80 mole MgO
0.172 mole $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
1.67 moles NaOH
(per liter of waste)

Fig. 2.5. Metaborate-Metaphosphate Glasses Incorporating Purex Waste Oxides.

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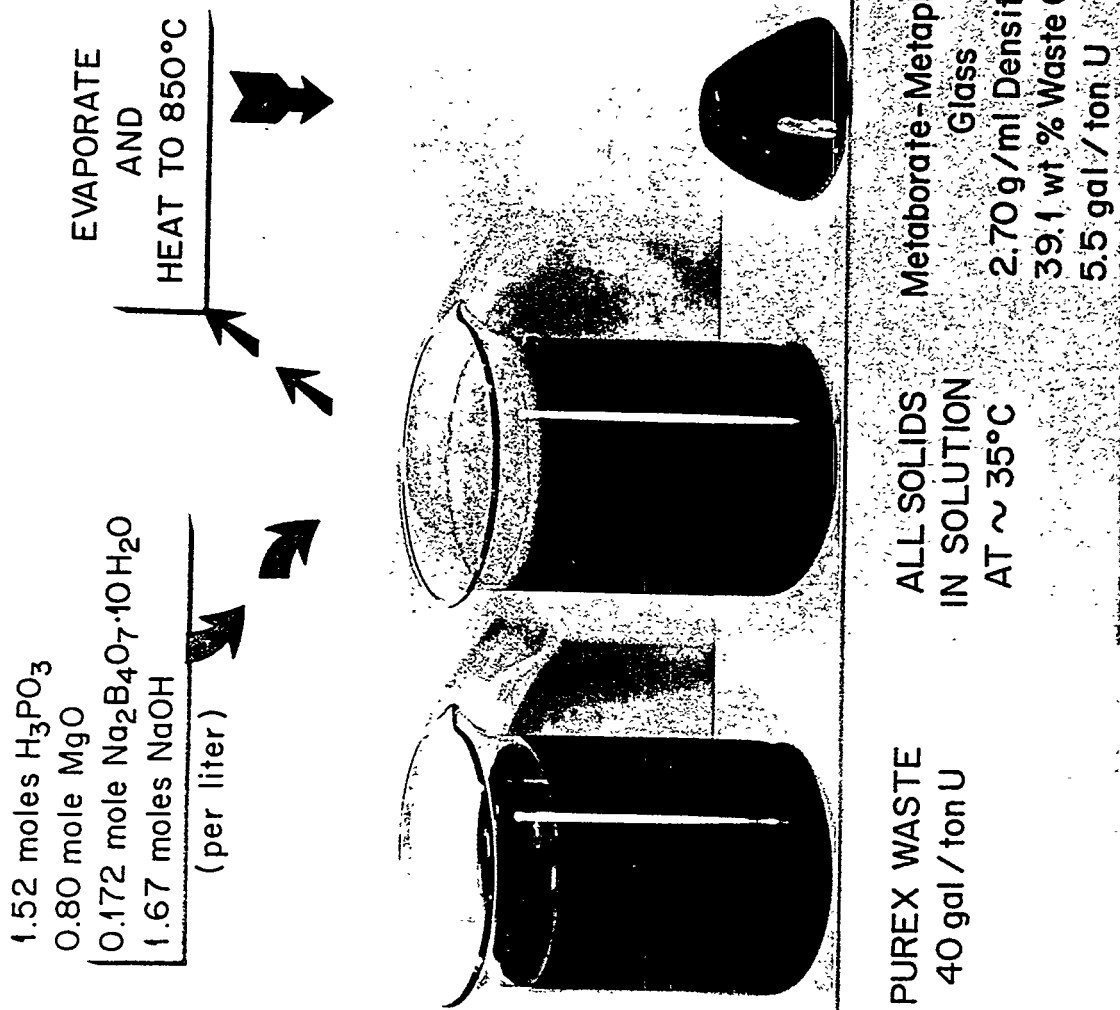


Fig. 2.6. Preparation of Metaborate-Metaphosphate Glasses Incorporating Purex Waste Oxides.

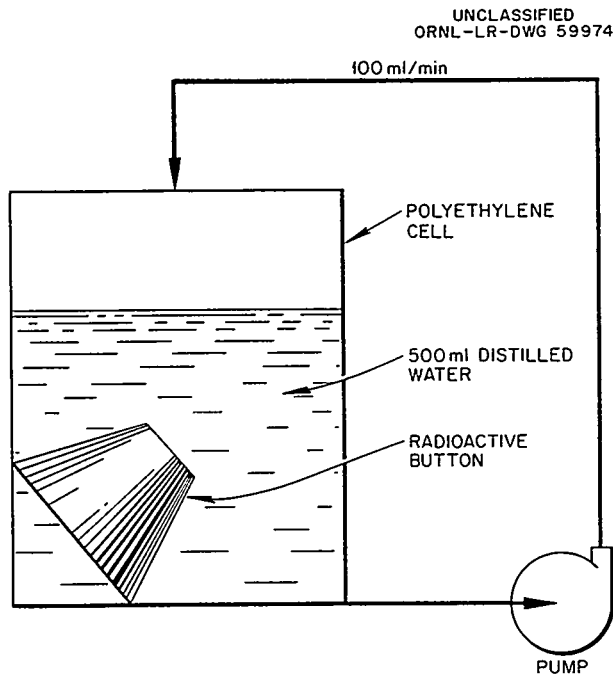


Fig. 2.7. Schematic of Apparatus for Leaching of Radioactive Glass Samples.

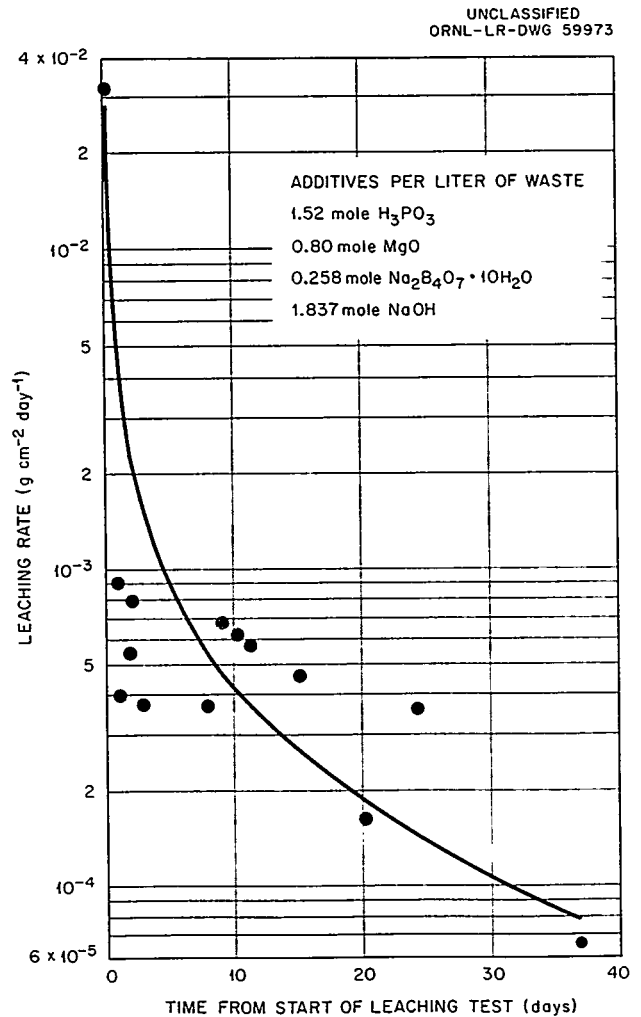


Fig. 2.8. Leaching Rate of Glass Incorporating Purex Waste Oxides and Sulfates. Purex Waste Composition (M): 6.1 NO_3^- , 5.6 H^+ , 1.0 SO_4^{2-} , 0.6 Na^+ , 0.5 Fe^{3+} , 0.1 Al^{3+} , 0.01 Cr^{2+} , 0.01 Ni^{2+} , 0.002 Ru .

The samples were counted for Cs-137 on the same gamma scintillation counter used in determining the cesium counts in the original spiked mixture. In calculating leaching rates, it was assumed that the activity is uniformly distributed throughout the glass.

2.2.3 Ruthenium Volatility

Previous work showed that volatilization of the ruthenium during calcination or fixation can be decreased and essentially eliminated by addition of reducing agents (4,7,8). For example, 20-40% of the ruthenium present was volatilized from Purex waste when calcined to 500°C without addition of any reducing agent. Operation under an atmosphere of NO reduced the ruthenium volatility to 1-3% under otherwise similar conditions. Addition of as much as 1.52 M orthophosphite (HPO_3^-) to the Purex, Darex, and TBP-25 waste solutions prior to batch calcination decreased the ruthenium volatility to or below the analytical background ($\sim 0.03\%$) (4). As little as 0.1 M phosphite prevented ruthenium volatility from Purex solution during batch evaporation until the temperature reached or exceeded 200°C. When no more phosphite was added, a total of 2-3% of the ruthenium could then be volatilized during calcination. The use of phosphite for controlling ruthenium volatility is particularly attractive since it is oxidized to phosphate, a fluxing agent.

Two experiments were performed to study the effect of the amount and time of phosphite addition on ruthenium volatility and noncondensable off-gas production during evaporation-fixation. The experiments were carried to about 500°C in small all-glass equipment (Fig. 2.9). A simulated high-activity Purex waste (Table 2.5) containing 0.184 g/liter stable ruthenium and 0.1 $\mu\text{C}/\text{ml}$ Ru-106 tracer was used. In each experiment the feed and/or additives were added continuously to the 200-ml evaporator flask, maintained about half-full, at a rate approximately equal to the boiloff rate, 1 ml/min. At the end of the feeding period, the material in the flask was evaporated to dryness and the residue heated to 500°C. The vapors from the flask passed through a downdraft condenser and the condensate was collected in 10-ml fractions. The noncondensable off-gas from the system was passed through four water-filled bubblers in series. The gas was pulled through the bubblers and pushed back to the flask with a Sigmamotor tubing pump. The individual condensate samples were analyzed for Ru-106 in a gamma scintillation counter. The residue was analyzed by gamma counting after dissolution in refluxing 12 M HCl. The equipment was washed by boiling 15 M HNO_3 through it. At the beginning of each experiment the system was flushed with argon to remove oxygen and nitrogen, which could complicate interpretation of off-gas analyses.

Phosphorous acid (H_3PO_3) was added to the system to decrease ruthenium volatility and MgO to decrease sulfate volatility. Monobasic sodium phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) and borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) were added as fluxing agents. The solution fed to the evaporation was Purex waste (Table 2.5) to which had been added, in moles/liter, 0.40 H_3PO_3 , 1.12 $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 0.80 MgO , 0.13 borax, and 0.46 NaOH , and in

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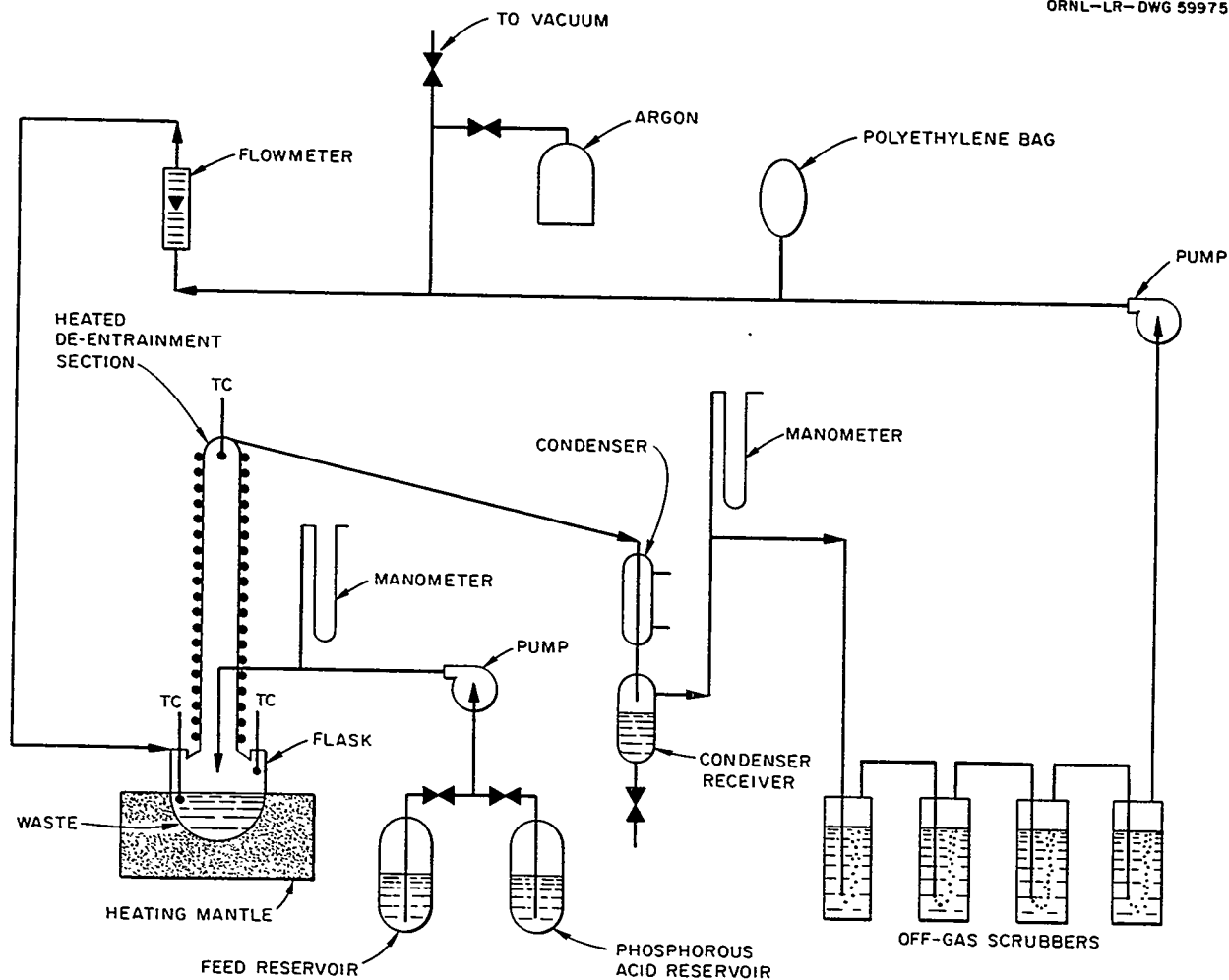


Fig. 2.9. Schematic of Apparatus for Studying Effect of Phosphorous Acid on Ruthenium Volatility During Evaporation-Calcination in Glass Equipment.

the second, 0.1 H_3PO_3 , 1.12 $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 0.80 MgO , 0.13 borax, and 0.46 NaOH . At the end of the feeding period in the second experiment sufficient 6 M H_3PO_3 was pumped into the evaporator that the total H_3PO_3 per liter of waste was 0.40 mole. That is, in the two experiments the total amount of each chemical added to the flask was the same, only the mode of adding the H_3PO_3 was different.

In the first experiment, the ruthenium material balance was 98.95%. The residue, equipment washings, condensate, and scrub liquid contained 85.47, 8.56, 4.92, and 0.00%, respectively, of the original ruthenium. In the second experiment, the equipment washings, condensate, and bubblers contained 1.04, 1.38, and 0.00%, respectively, of the original ruthenium. The residue was not analyzed since the flask cracked at the end of the experiment. No net off-gas was produced in either case.

Earlier results (4f) showed that ruthenium volatility can be decreased to background levels, 0.03%, when 1.52 moles H_3PO_3 is added per liter of Purex waste. The results above, 1.38-4.92% Ru volatilized, indicate that the ruthenium volatilized depends not only on the total H_3PO_3 added but also on when during the evaporation the H_3PO_3 is added. The bulk of the phosphorous acid appears to be needed at the higher temperatures, 150-500°C, when the nitrate salts in the waste begin to decompose.

2.3 Design of Calcination Pilot Plant (J. O. Blomeke, J. M. Holmes)

As a result of a preliminary design study and cost estimate (9), it has been proposed that a waste calcination pilot plant for demonstration of both the pot and BNL rotary calciners be installed in three of the five existing cells of the ICPP hot pilot plant at an estimated cost of \$1,000,000. The two calciners require the same feed, off-gas decontamination, and mechanical handling equipment and can be tested with TBP-25 waste now on hand at ICPP as well as with Thorex, Purex, and Darex type wastes which may later be available or be prepared for this demonstration. In addition, the equipment can ultimately be used to demonstrate the fixation of wastes in phosphate glasses. Discussions with Phillips personnel are in progress to define objectives and responsibilities. It is expected that the conceptual design of this plant will start in July 1961 and be followed by detailed design and procurement in the latter half of FY-62.

Design of mechanical equipment for the calciners has been started with the objective of developing a mockup that will demonstrate such remote operations as calciner positioning, connecting, sealing, and storage. These features will be tested at the Georgia Nuclear Laboratories, Dawsonville, Georgia, where hot cell mockup facilities and manpower are immediately available. A permanent mechanical mockup will be built in Idaho after completion of the feasibility testing at GNL.

3.0 LOW-LEVEL WASTE TREATMENT

A scavenging-ion exchange process (3f,6,10,11) is being developed for decontaminating the large volumes of slightly contaminated water produced in nuclear installations; ORNL low level waste is being used as a medium for study. The scavenging-ion exchange process uses phenolic resins, as opposed to polystyrene resins, since the phenolic resins are much more selective for cesium in the presence of sodium; i.e., the Cs/Na separation factor is 160 for CS-100 or C-3 resin vs. 1.5 for Dowex 50 resin. Other cations, e.g., strontium and rare earths, are also sorbed efficiently. Inorganic ion exchange media such as vermiculite and clinoptilolite are being studied as alternative ion exchange media. The waste solution must be clarified prior to ion exchange since ion exchange media do not remove colloidal materials efficiently. Water clarification techniques are being developed for both the ion exchange processes and for the ORNL Lime-Soda process waste water treatment plant. Work is proceeding on both development and pilot plant programs.

3.1 Scavenging-Ion Exchange Process (W. E. Clark, R. R. Holcomb)

In the scavenging-ion exchange process, the water is made 0.01 M in NaOH (pH ~11.7), with 5 ppm of iron to form a floc, which settles and removes all suspended material and carries significant fractions 50-99% of the rare earths, cobalt, ruthenium, and zirconium for which the succeeding ion exchange step is less effective (Table 3.1, Fig. 3.1). After settling and filtration, the water is passed through a CS-100 ion exchange resin column where >99.9% of the cesium and strontium are sorbed during the passage of 2000 resin bed volumes of water. At pH 12, a large fraction of the phenolic groups on the CS-100 resin (phenolic-carboxylic type) are ionized and free to sorb cations. As a result of the two steps the radioactivity content of ORNL waste would be decreased to ~10% of the maximum permissible concentration. The activity is eluted from the resin with dilute nitric acid and the acid recovered by evaporation. The combined dry volume of evaporator salt residue and flocculation cake is about 0.6 vol, i.e., about 0.03 vol % of the treated water. The flowsheet in Fig. 3.1 represents a vast improvement over that previously published (10b) in that (1) CS-100 resin rather than C-3 resin is used, (2) nitric acid rather than hydrochloric acid is the regenerant, and (3) only 0.1 as many equivalents of acid are required for elution. The elimination of hydrochloric acid has a double advantage. Not only is a special HCl-resistant still eliminated, but also existing conventional nitric acid stills can be used at most installations.

A small pilot plant facility was constructed and operated for three runs (Fig. 3.2). In the first run, in which 1150 resin bed volumes of water were processed over a 115-hr period, the pretreatment steps of flash mixing, flocculation, and sludge blanket clarification did not produce sparkling water; thus, the burden of clarification was placed on the filters. For the second (72 hr, 1400 bed volumes) and third (111 hr, 1900 bed volumes) runs, an anthracite bed was installed to promote longer filter life, and the design of the sludge blanket clarifier was changed to improve sludge distribution. The results were

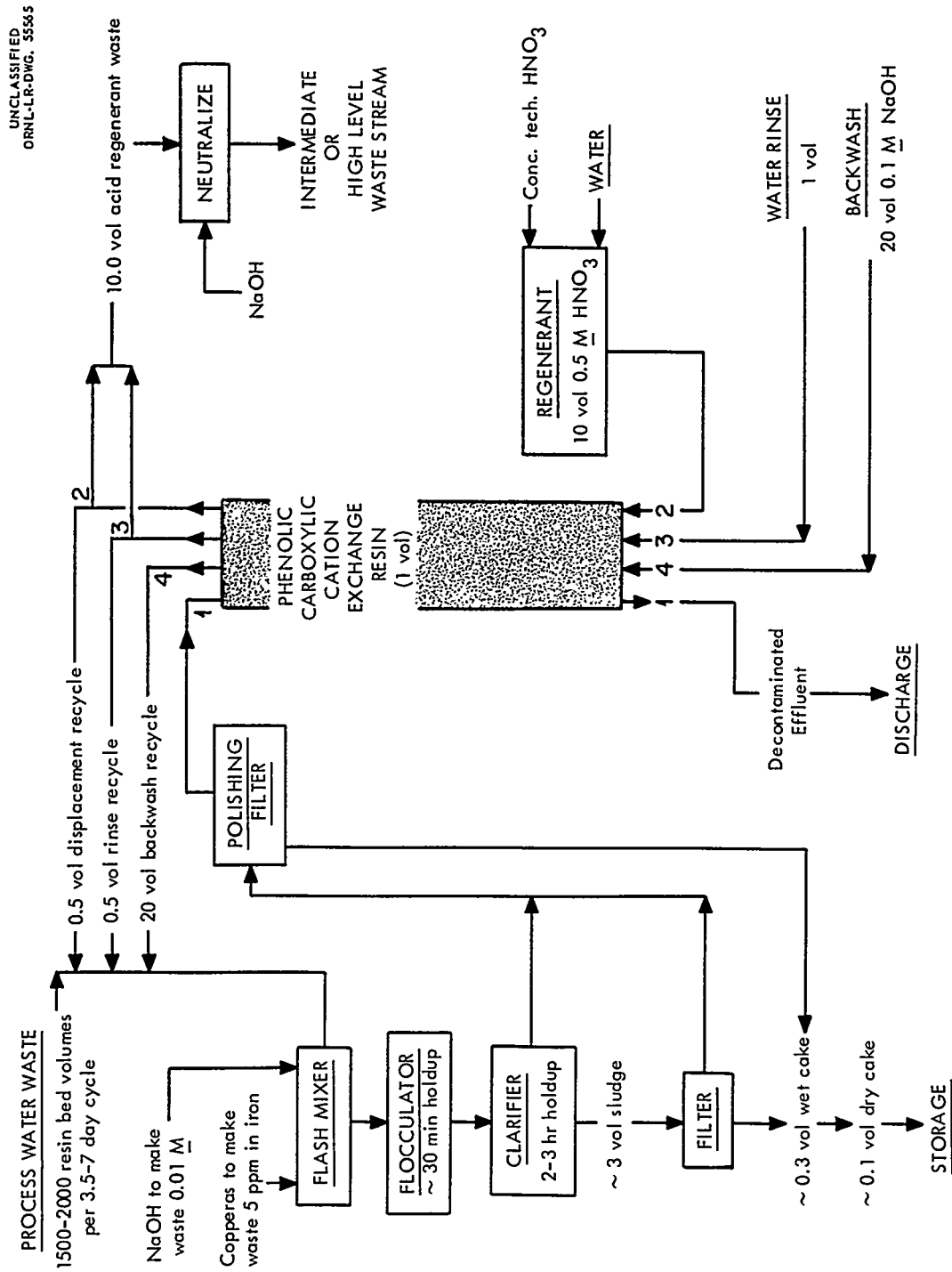


Fig. 3.1. Process Water Decontamination with Carboxylic-Phenolic Ion-Exchange Resin.

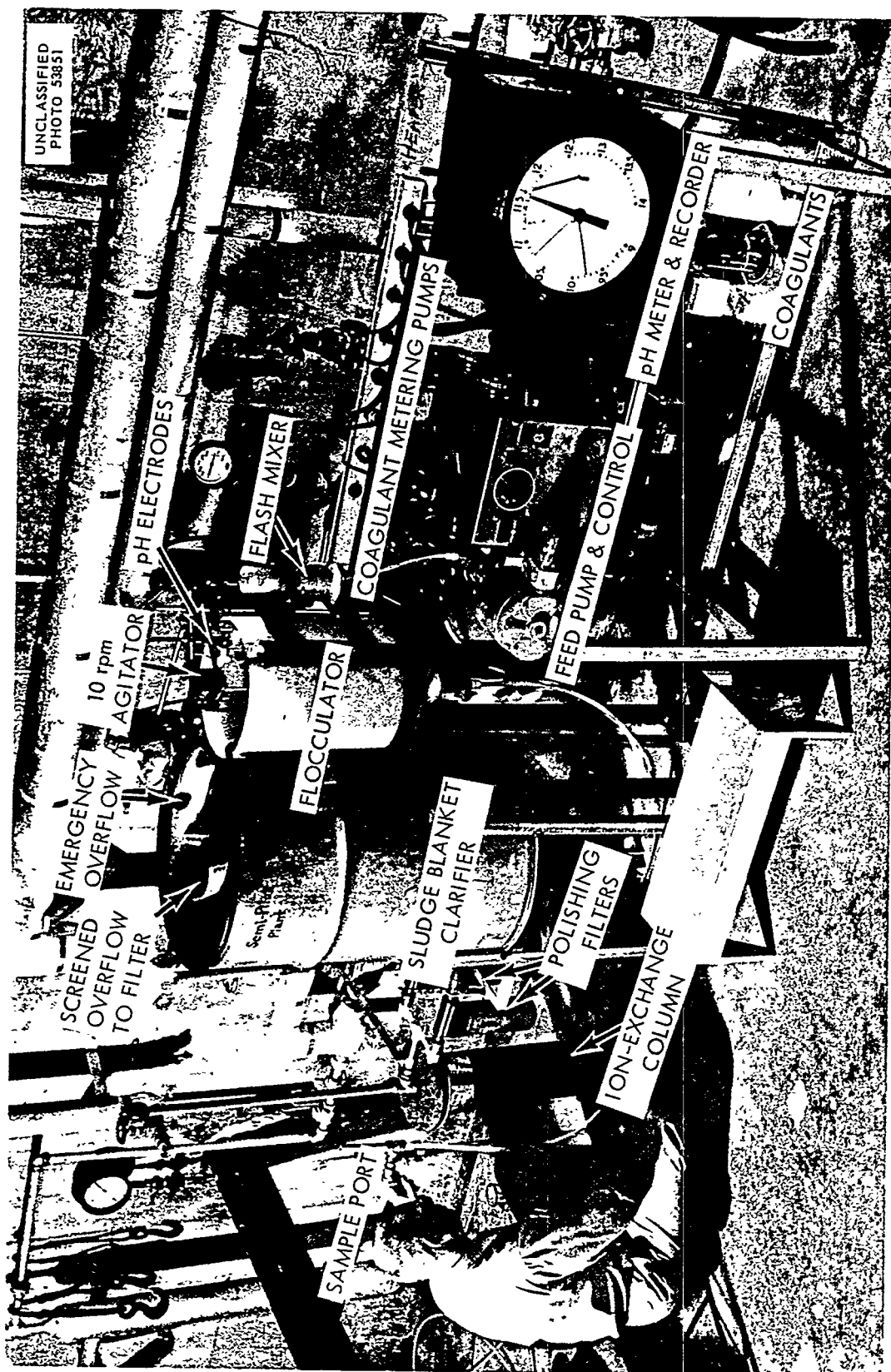


Fig. 3.2. Semi-Pilot Plant for Demonstration of Ion-Exchange Treatment of Low Level Process Waste Water.

Table 3.1 Decontamination of ORNL Low-Level Waste by the
Scavenging-Ion Exchange Process; Laboratory Scale Tests

Activity	Activity Removed by Precipitation- Filtration (% of original)	Activity Removed by Ion-Exchange (% of remaining)	Typical Overall Process D.F.'s
Cs	1-10	> 99.9	1000
Sr	~50	> 99.9	1000
Ce and other RE's	90-99	10	100
Co	70-95	10	10-40
Ru	70-90	10	10
Zr-Nb	50		

excellent and the settler overflow water produced had only 3 ppm turbidity and 8 ppm total dissolved hardness as CaCO_3 compared to 40-50 ppm turbidity and 56 ppm total hardness in the first run. Under these conditions no more than two and perhaps only one filter backwash per three-day cycle will be required. Radiochemical analyses (Table 3.2) for runs 1 and 2 confirm the results obtained in laboratory studies, i.e., decontamination factors for strontium and cesium ≥ 1000 , decrease of gross activity to 54% of the mpc for gross unknown activity assuming 100% Sr-90 for a 168-hr week, and decrease of strontium and cesium to $\leq 1.0\%$ of the mpc for a 168-hr week. As expected, decontamination from cobalt and ruthenium was low. Improvement of decontamination from ruthenium and cobalt will be the subject of future studies. On termination of the loading cycle, the resin was eluted upflow with 10 bed volumes of 0.5 M HNO_3 , producing a typical elution curve (Fig. 3.3). The acid eluant was then evaporated, resulting in a volume reduction of 30 to 1 without solids formation. On this basis the overall volume reduction factor was ≥ 3000 .

In addition to synthetic organic ion exchange resins, other exchange media are being studied on a laboratory scale to determine their relative efficiencies for treatment of low-level waste. Greater than 99.9% (d.f. = 1000) of the cesium and strontium were removed from 6900 bed volumes of ORNL low-level waste with 19.2 ml of clinoptilolite, a naturally occurring zeolite mineral. The column diameter was 0.5 in. and the flow rate $20 \text{ gal ft}^{-2} \text{ hr}^{-1}$. This represented a breakthrough level of 1% of the feed activity concentration. About 8700 volumes had passed through at the 50% breakthrough level. The breakthrough was attributed entirely to cesium, strontium could not be detected in any of the effluent samples.

3.2 Design of Scavenging-Ion Exchange Pilot Plant (J. O. Blomeke, J. M. Holmes)

A pilot plant is being installed for a demonstration of the cleanup of ORNL process waste by scavenging and ion exchange. The plant is sized for a capacity of 10 gpm, or 1/50 of that required to handle the entire waste stream at a capital cost of \$65,000. It will contain the following major items of equipment (Fig. 3.4): a 3.3-gal flash mixer (W-11), 300-gal flocculator (W-12), 1870-gal clarifier (W-13), 7.1-ft² Eimco Burwell polishing filter (W-17), ion exchange column with bed 10 in. dia x 8 ft long (W-18), ion exchange column with bed 18 in. dia x 34 in. long (W-19), 650-gal caustic storage tank (W-20), and two 900-gal glass-lined regeneration acid tanks (A-10, A-11). Provisions have been made to install an HCl evaporator system (A-12, A-13, A-14) later if it should become desirable to demonstrate the process with HCl regeneration. The present schedule calls for cold startup of this plant in August 1961.

The flash mixer-flocculator-clarifier combination is designed to remove at least 90% of the initial feed turbidity plus the solids precipitated by the addition of NaOH and coagulant to the feed (pH 11.7). The polishing filter will decrease the level of undissolved solids to < 0.2 ppm. It will also demonstrate filtration of the clarifier sludge during shutdown. Two ion exchange beds (1/50 of plant scale volume) will be tested separately. The 10-in. dia x 8-ft-high bed is scaled down at constant liquid velocity

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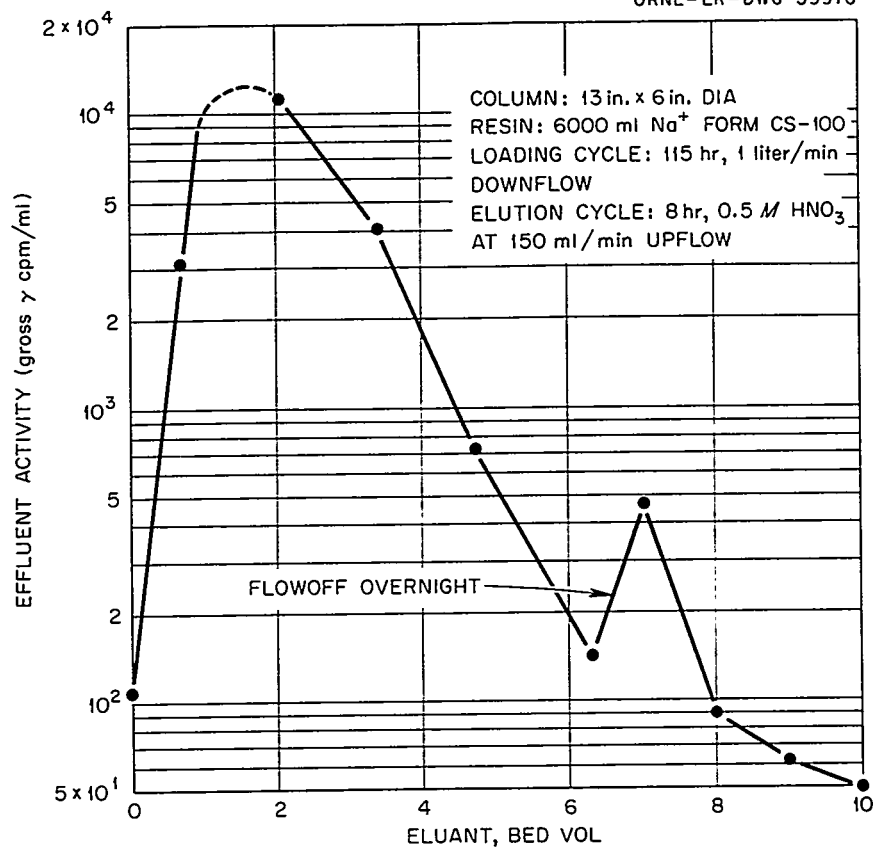
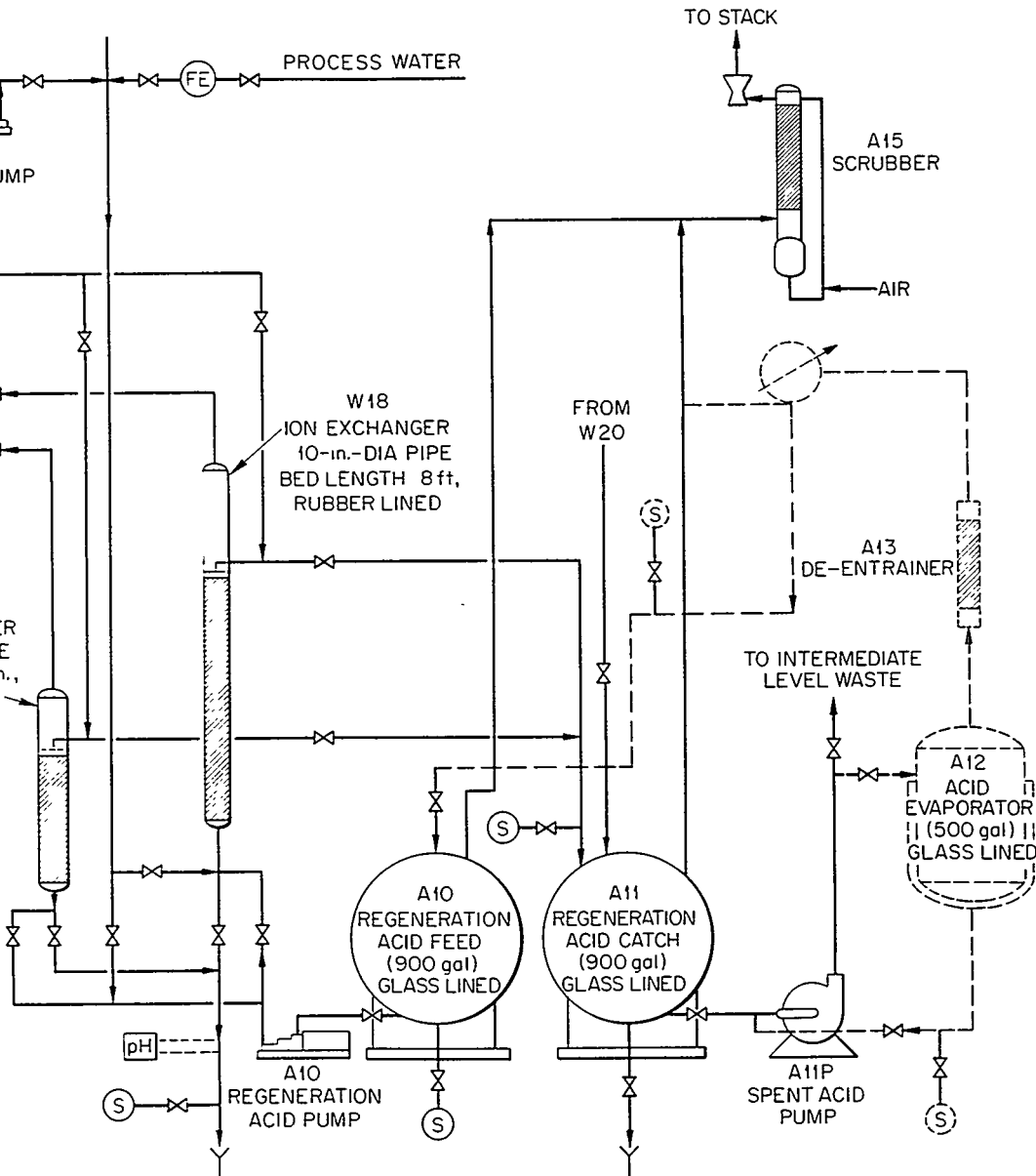


Fig. 3.3. Elution of Duolite CS-100 Resin with 0.5 M HNO₃ After Exhaust ORNL Low-Level Waste.



-Treatment Pilot Plant.

Table 3.2 Decontamination of ORNL Low-Level Waste by the
Savenging-Ion Exchange Process; 60 liters/hr Pilot Plant Tests

Code	Radiochemical						
	Gr β (c ml ⁻¹ min ⁻¹) (9.6% geometry)	TRE β (c ml ⁻¹ min ⁻¹) (22.3% geometry)	Sr β (d ml ⁻¹ min ⁻¹)	Gamma Spectrometry (d ml ⁻¹ min ⁻¹)			
				Ru-106	Cs-137	Zn-65	Co-60 Zr-Nb-95
SPP run 1							
Feed	28	27	92	6.6	20	7.4	5.4
Effluent (300 bed vol)	1.1	0.17	0.02	2.1	None detected	None detected	2.1
SPP Run 2							
Feed	35.3	32	94	6.5	21	Trace	4.6 10
Effluent (1398 bed vol)	1.3	0.3	0.04	1.8	None detected	None detected	2.4 None detected

The results of the plant tests to date are summarized in Table 3.4. The efficiency of plant operation was lower during the October test because of a slowly settling floc, and substantial quantities of solids appeared in the plant effluent. In another test, to determine the proper concentration and point of addition of coagulant aids, introduction of 1.0 ppm of Hagan 323 before the flash mixer and 2.0 ppm of Hagan 2 to the flash mixer improved solids removal considerably. The average concentration of suspended solids in the effluent in the May test was 15 ppm, and the results of analyses of filtered and unfiltered samples showed the radionuclides associated principally with the liquid phase.

Earlier plant tests showed that removals of strontium and cesium can be increased for short periods of time, when needed, by optimizing the amounts of lime, soda ash, and clay. However, as a routine practice, it is not desirable to optimize the chemical dosages because this increases the volume of sludge. Coagulant aids, adding only \$0.01 to \$0.02 per 1000 gal to the cost of treatment, will improve the clarity of the plant effluent and increase plant efficiency. The addition of phosphates will also improve plant efficiency, but adds to the cost of treatment by about \$0.16 per 1000 gal. To obtain overall removals > 95% routinely, second-stage treatment is necessary.

Table 3.4 Process Waste Water Treatment Plant Tests

	Vol Treated (gal x 10 ⁶)	Amount Removed (%)		
		Gross β	Sr-89-90	Cs-137
August 22, 1960 to October 9, 1960 ^a	23.1	77	77	79
October 10, 1960 to October 16, 1960 ^b	3.3	78	67	78
March 20, 1961 to April 30, 1961 ^a	12.3	77	79	85
May 2, 1961 to May 7, 1961 ^c	1.7	96*	87	97
		97**	89	98

^aLime stoichiometric, soda ash 200 ppm excess, clay 200 ppm; effluent sample not filtered.

^bSame as (a) with addition of 130 ppm PO₄; operating rate 330 gpm; effluent sample not filtered.

^cSame as (a) with addition of 125 ppm PO₄, 1.0 ppm Hagan 323, and 2.0 ppm Hagan 2; operating rate 200 gpm; *effluent sample not filtered; **effluent sample filtered.

from the proposed plant bed. The 18-in.-dia x 32-in.-high bed has the same length/diameter ratio as the proposed plant and will determine if the data obtained from the 8-ft bed must be corrected for a lower length/diameter ratio when scaling up to the plant bed size. About 72 hr should be required to exhaust one of the beds.

The ion exchangers will be regenerated by feeding acid upflow to the beds followed by a water and caustic wash to convert the resin to the sodium form. Activity removed by the beds will be returned to the settling basin or sent to the concrete waste tanks.

3.3 Process Waste Water Treatment Plant (K. E. Cowser)

3.3.1 Phosphate Coagulation

The successful experience in other countries with phosphate coagulation for the removal of strontium from low-level liquid wastes, and the possibility of increasing strontium removal from ORNL process waste by the formation of apatite in the existing CaCO_3 process waste water treatment system, prompted an investigation of the use of phosphates. Previous studies of phosphate coagulation had demonstrated the need for close control of pH and of the $\text{PO}_4^{=}/\text{Ca}^{++}$ ratio in the waste (12-16). Nesbitt (13) found that strontium removal decreased as the pH increased from 10.4 to 11.4, presumably due to the presence of small quantities of a stable calcium phosphate sol in the supernatant liquid. Centrifugation of the settled supernatant removed most of the stabilized material.

The variable chemical quality of ORNL process waste, the lack of a recording pH meter at the plant, and the single-stage treatment facility in operation suggested the use of phosphates as a supplement to the normal lime-soda softening treatment rather than as a replacement for the present system. Tap water spiked with Sr-85 was treated with various amounts of phosphate, by a jar test procedure, to duplicate the contact time and agitation sequence of the treatment plant (17). Strontium removal was maximum at about 125 ppm of $\text{PO}_4^{=}$ (Fig. 3.5a) with little difference noted whether the phosphates were added during flash mixing or after 11 min of flocculation. A phosphate concentration above 200 ppm hindered settling of the flocculent material; in all cases the floc formed was easier to resuspend by slight agitation than those when only CaCO_3 was used.

The removal of strontium by primary phosphate coagulation with various $\text{PO}_4^{=}/\text{Ca}^{++}$ ratios was compared to that of lime-soda softening with 95 ppm and 125 ppm of phosphate added (Table 3.3). For effective removal of strontium by phosphate coagulation, it was necessary to adjust the pH of the system. At pH 10.2, the removal of strontium was increased by filtering the supernatant. Lime-soda softening with added phosphate did not require adjustment of pH, produced a floc of better settling character, and removed as much strontium as the most efficient straight phosphate treatment.

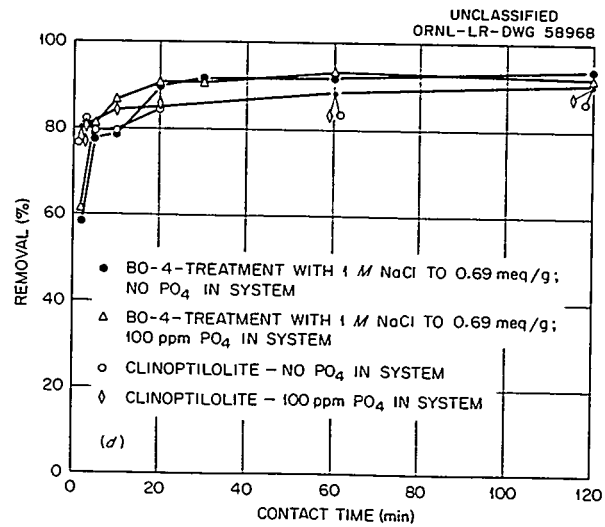
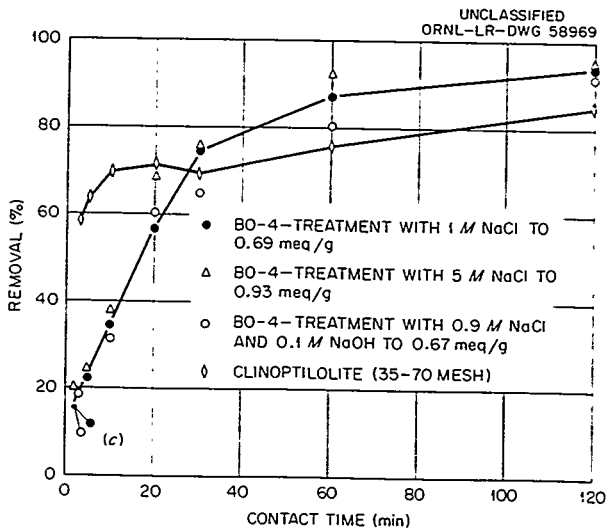
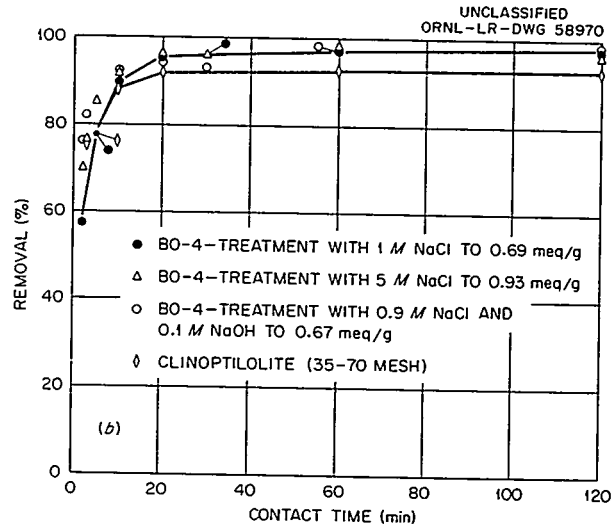
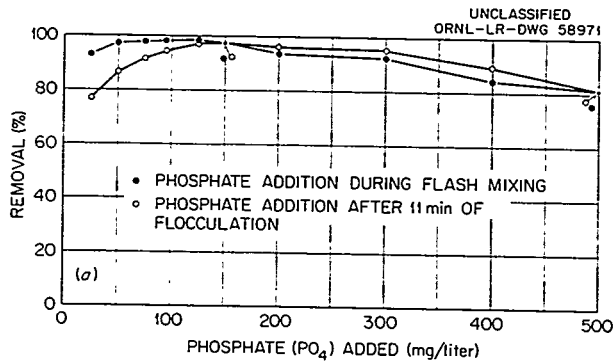


Fig. 3.5. Effect of Phosphates on (a,b,c) Strontium Removal and (d) Cesium Removal.

Table 3.3 Comparison of Phosphate Coagulation with Lime-Soda Softening and Supplemental Phosphate on Strontium Removal

Phosphate (ppm)	$\frac{\text{PO}_4}{\text{Ca}^{++}}$	pH	Sr Removal (%)			
			No pH Adjustment		pH Adjusted to 10.2	
			Settling	Settling + Filtration	Settling	Settling + Filtration
47.4	1.6 ^a	8.8	51.0	53.8	72.6	66.5
63.4	2.1	9.0	58.7	61.5	85.3	78.0
69.5	2.3 ^b	9.1	71.7	74.4	80.0	94.1
85.9	2.9 ^c	9.3	81.1	83.0	82.6	97.2
147.4	5.0 ^d	9.8	95.4	96.0	83.1	99.0
95 ^e	--	10.4	96.3	97.7	--	--
125 ^e	--	10.4	96.4	97.5	--	--

^aStoichiometric amount of phosphate and calcium.

^bOptimum PO_4/Ca ratio according to Lauderdale (12).

^cOptimum PO_4/Ca ratio according to Nesbitt (13).

^d100 ppm excess PO_4 .

^eStoichiometric lime, 200 ppm excess soda ash, 200 ppm clay.

In anticipation of difficulty in obtaining a settleable floc during test operations in the treatment plant, a number of coagulant aids were investigated. These included FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$, $\text{Th}(\text{NO}_3)_4$, additional clay, and Hagan aids 2, 18, 50, and 323. * A combination of 0.5 to 1.0 ppm Hagan 323 and 1.0 to 2.0 ppm Hagan 2 gave the best results.

To determine the optimum combination of lime, soda ash, clay, and phosphate for the most effective removal of strontium and cesium, a series of laboratory tests with actual process waste was started. The same experimental procedure was used as that previously applied to lime-soda softening (18). The most effective combination of treatment variables used thus far (lime 0.83 times stoichiometric, soda ash 200 ppm excess; phosphate 250 ppm, clay 117 ppm) removed 99.0% of the strontium and 87.7% of the cesium.

* Hagan Chemicals and Controls, Inc., Pittsburgh

3.3.2 Natural Minerals for Second Stage Treatment

The use of natural minerals as sorptive material for second-stage treatment of ORNL process waste is predicated on their ability to sorb and retain radionuclides and on the safety and economy of ultimate disposal of the contaminated solid without additional treatment. Regeneration and re-use of mineral columns would not be necessary, because of their low cost, if the total volumes of minerals required are relatively small.

To assess the suitability of various natural minerals for column operation after the clarification step, the quantity of strontium and cesium removed and the rates of removal were evaluated by slurry tests. Of the minerals tested, vermiculite ore is one of the most promising with respect to efficiency, availability, and cost (Table 3.5). Small quantities of the minerals were contacted for various times with 30 ml of a synthetic waste typical of the effluent from the ORNL treatment plant. A phosphate-treated waste was simulated by addition of 100 ppm of phosphate.

It is necessary to pretreat raw vermiculite and remove the readily replaceable calcium and magnesium, thus preventing their later interference with column operation. Sodium chloride is effective for this pretreatment and distribution coefficients of 5000 and greater are shown by BO-4, Na-treated vermiculite.* The presence of 100 ppm of phosphate interfered with strontium removal by all minerals tested, but had a negligible effect on cesium removal. From control systems where no phosphate was added, removal by vermiculite and clinoptilolite of about 95% of the strontium was rapid (Fig. 3.5b), an important factor in effective column operation; after 30 min contact time there was little additional removal of strontium.

Phosphates inhibited the rate of strontium removal by both vermiculite and clinoptilolite, but not as severely in the case of clinoptilolite (Fig. 3.5c). The rate of cesium removal by vermiculite and clinoptilolite was not affected when phosphates were present (Fig. 3.5d).

These natural minerals appear to have application in waste treatment. To demonstrate the extent and limitation of their use in second-stage treatment of ORNL process waste, laboratory-scale columns are being evaluated and a pilot plant, capable of treating up to 3 gpm of treatment plant effluent, is under construction.

4.0 ENGINEERING, ECONOMIC, AND HAZARDS EVALUATION

J. O. Blomeke, R. L. Bradshaw, J. J. Perona, J. T. Roberts

A comprehensive study has been undertaken to evaluate the economics and hazards associated with alternative methods for ultimate disposal of highly radioactive liquid

* Zonolite Company, Travelers Rest, South Carolina

Table 3.5 Cesium and Strontium Distribution Coefficients* Between Effluent of Process Waste Treatment Plant and Sorbents

Waste composition: 8.0 ppm Ca^{++} , 2.9 ppm Mg^{++} , 235 ppm Na_2CO_3 , 100 ppm $\text{PO}_4^{=}$ where indicated.

Material	Cesium				Strontium			
	Na Treated		Natural		Na Treated		Natural	
	100 ppm PO_4	No PO_4	100 ppm PO_4	No PO_4	100 ppm PO_4	No PO_4	100 ppm PO_4	No PO_4
Vermiculite BO-1		180		300				
Vermiculite BO-2	170	180		340	110	60		40
Vermiculite BO-3	1100	1200			430	2700		
Vermiculite BO-4								
1 M NaCl	3200	5000			4700	13,000		
0.9 M NaCl, 0.1 M NaOH					3400	22,000		
5 M NaCl					6100	14,000		
Vermiculite BE-3						6000		
Clinoptilolite	3700	3200	2900	2700	280		1700	3900
Rock Phosphate			2900	2900				
Fine							300	400
Coarse							130	
Al_2O_3							300	700
Bauxite							490	1600

* Distribution coefficient (2 hr contact time) = radionuclide sorbed per gram of material ÷ radionuclide unsorbed per milliliter of solution.

and solid wastes. Such an evaluation is a necessary prerequisite to a meaningful experimental study of radioactive waste disposal. All steps between fuel processing and ultimate storage will be considered, and the study should define an optimum combination of operations from the many available. Conceptual designs of ultimate storage methods, which must be made for cost estimation purposes, should be a valuable guide to later experimental programs.

A 6-tonne/day plant is assumed, processing 1500 tonnes/year of uranium converter fuel at a burnup of 10,000 Mwd/tonne and 270 tonnes/year of thorium converter fuel at a burnup of 20,000 Mwd/tonne. This hypothetical plant would be processing all the fuel from a 15,000-Mw_e nuclear economy, which may be in existence by 1970. The preliminary operations to be evaluated are interim liquid storage, conversion to solids by pot calcination, interim storage of solids in pots, and shipment as either liquids or calcined solids. The ultimate disposal methods to be evaluated are calcined solids in salt deposits, in vaults, and in vertical shafts and liquids in salt deposits, in deep wells, by hydrofracture, and in tanks.

A cost study of interim liquid storage was completed. Costs for storage of acidic Purex (50 gal/tonne of uranium processed), neutralized Purex (60 gal/tonne), acidic conventional Thorex (400 gal/tonne) and neutralized Thorex (640 gal/tonne) wastes were estimated for storage times of 0.5 to 30 years. Tanks of Savannah River design were assumed, with stainless steel construction for acidic wastes and mild steel construction for neutralized wastes. Stainless steel and zirconium decladding wastes were assumed to be stored separately from the high-level wastes. The costs of intermediate-level waste disposal will be assessed later.

For the high-level wastes, with interim storage time defined as filling time plus full time (equivalent to average liquid residence time if emptying time is equal to filling time), tank costs were minimum when the full time was roughly 75% of the interim storage time, at present worth considerations. For waste storage times of 0.5 to 30 years, costs ranged from 2.0×10^{-3} to 9.3×10^{-3} mill/kwh_e for storage of acid wastes and from 1.5×10^{-3} to 4.7×10^{-3} mill/kwh_e for alkaline wastes. Details of this study are given in ORNL-3128 (in press).

A cost study of conversion to solids by pot calcination is in progress. Costs of the calcination plant building as a function of building size, which varies for different combinations of acid and alkaline wastes and pot diameters, and as a function of shielding wall thickness, which varies according to the length of interim liquid storage, were estimated. Processing equipment costs were also estimated. Estimates of the operating costs, including costs of calcination vessels, are not yet complete. Seven waste types were considered: (1) acidic Purex, 7 gal of porous solids per tonne of uranium; (2) neutralized Purex, 13.5 gal of dense solids per tonne; (3) neutralized Purex with the calcination vessel filled twice; (4) acid deficient conventional Thorex, 60 gal of porous solids per tonne of thorium; and (5) acidic Thorex waste plus additives, 78 gal of a glass, similar to that described in AERE-R3610, per

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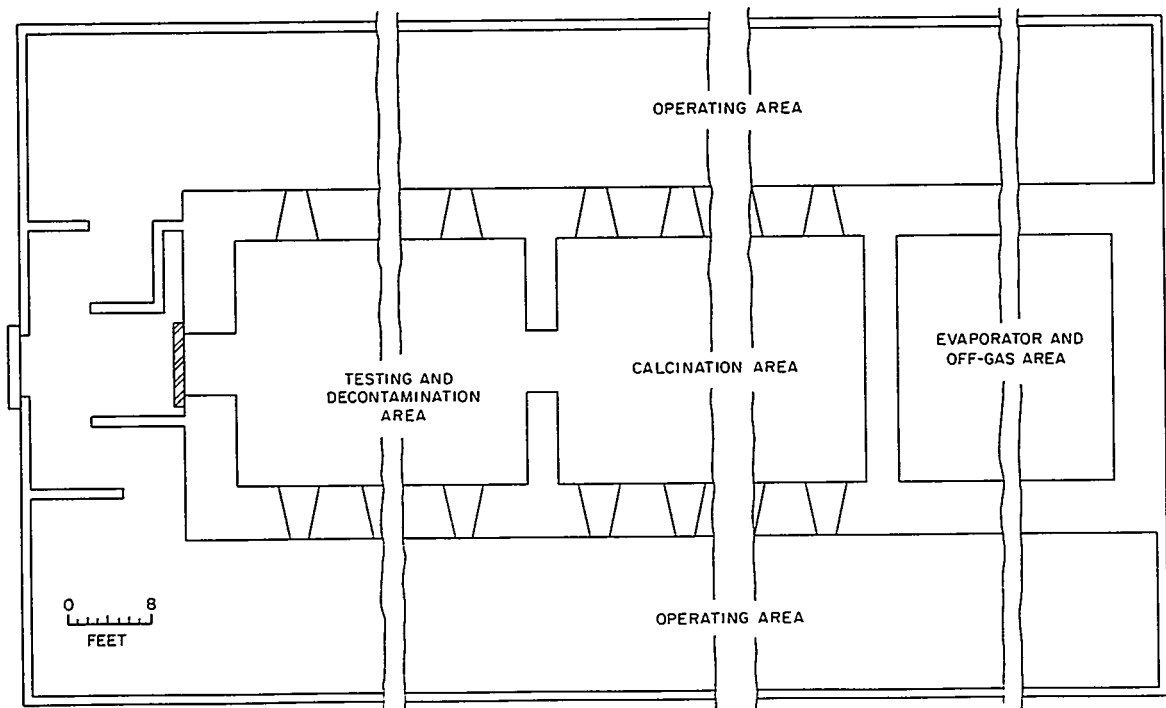


Fig. 4.1. Plan View of Calcination Plant Layout.

tonne; (6) neutralized Thorex, 264 gal of dense solids per tonne of thorium; and (7) neutralized Thorex with the vessels filled twice. The neutralized wastes melt during calcination when the temperature of the solids is raised to 900°C. After this melting, only the lower half of the calcination vessel is occupied, so that a second filling could be performed to improve utilization of space in the vessels. The second filling would be accomplished, however, at the expense of a decrease in the average processing rate per furnace, since only half the heat transfer surface of the vessel would be available during the second filling.

Current ORNL pot calcination work is being done on TBP-25 and Darex type wastes, but these wastes were not included in the long-range study since the 6-tonne/day plant assumed does not process highly enriched fuels and since decladding wastes were assumed to be handled separately from the high-level wastes. For pot-calcination purposes, TBP-25 waste is not greatly different from conventional Thorex waste, however, and Darex waste is not greatly different from concentrated Purex waste.

The number of pot calcination lines to process each waste type was calculated for vessel diameters of 6, 12, and 24 in. except for the Thorex glass, in which case experimental rate data were available for only a 6-in.-dia pot. The required number of pot lines ranged from two for acid Purex waste in 12- or 24-in.-dia vessels to 16 for Thorex glass (Table 4.1). Calcination and changeout times of 3 and 8 hr were assumed for each waste type independent of vessel diameter. Internal heat generation is sufficiently high that 3 hr calcination is long enough, though longer periods are required with nonradioactive synthetic wastes now being studied (ORNL-3163, in press).

Table 4.1 Required Number of Pot Calcination Lines for 6-tonne/day Plant

Waste Type	No. of Processing Lines*		
	6-in.-dia Pot	12-in.-dia Pot	24-in.-dia Pot
Acid Purex	3	2	2
Neutralized Purex	8	4	3
Neutralized Purex filled twice	7	4	4
Acid deficient Thorex	4	3	3
Thorex Glass	16	-	-
Neutralized Thorex	13	7	5
Neutralized Thorex filled twice	13	7	6

* Includes 15 to 20% downtime.

The processing plant building was considered to be made up of three areas: calcination, evaporator and off-gas equipment, and testing and decontamination. The required plant floor area for calcination, assumed to be directly proportional to the number of pot lines and independent of pot diameter, was taken as 100 ft² per pot line. The required area for evaporator and off-gas equipment was assumed proportional to the square root of a plant throughput factor. Since the evaporator and off-gas equipment duty peaks sharply during the operation of a single pot line, the peaks were assumed to be staggered at equal time intervals, and the plant throughput factor was obtained from a normalized typical duty profile to which a coincidence factor was added as a conservative measure. A plant floor area of 200 ft² for a single pot line was assumed. The required plant floor area for decontamination and testing was taken as 100 ft² plus 9 ft² per pot for a 3-day production holdup.

Calculated total plant floor areas for all 108 combinations of Purex and Thorex waste types in vessels of the three diameters ranged from 1090 ft² for an acid Purex-acid Thorex plant with 24-in.-dia calcination vessels for both waste types to 3490 ft² for a neutralized Purex-acid Thorex glass plant with 6-in.-dia calcination vessels for both. Fractions of the three subareas correlated well with the total plant area and without regard to waste type or vessel size, so that three total plant areas spanning the range were chosen for cost estimation (Table 4.2) with costs of intermediate plant sizes to be obtained from a plot.

Table 4.2 Floor Areas of Pot Calcination Plants Chosen for Cost Estimation

Area Purpose	Area (ft ²)		
	Plant 1	Plant 2	Plant 3
Calcination	600	1380	1920
Evaporator and off-gas	360	460	480
Testing and decontamination	240	460	800
	<hr/> 1200	<hr/> 2300	<hr/> 3200

A plan sketch of the plant layout is shown in Fig. 4.1. Shielding calculations were made, showing that shielding wall thicknesses of 5 to 7.4 ft of ordinary concrete are required for processing Purex wastes decayed from 30 years to 120 days. Building costs were obtained by cost estimating the following items for each of the three plant sizes with 4-, 5-, 6- and 7-ft shielding walls: canyons, operating areas, zinc bromide windows, lead doors, stainless steel lining, bridge crane, sampling stations, cell ventilation and exhaust system (including stack), and site preparation and service facilities. Including

construction overhead (40%), engineering (15%) and contingency (20%), building costs ranged from $\$1.5 \times 10^6$ for a 1200 ft² canyon with 4-ft walls to 3.9×10^6 for a 3200 ft² canyon with 7-ft walls. Building costs were amortized over 50 years at 4% interest, resulting in annual costs ranging from \$72,500 to \$181,000.

Process equipment items were separated into two groups, those amortized over 20 years and those over 10 (Table 4.3). Furnaces were cost estimated at \$12,000 each regardless of diameter, since average processing rate during filling is independent of calcination vessel diameter. Model 550 General Mills manipulators with 3-ton hoists were specified at \$80,000 each. Annual costs for the 20-year items were \$63,700, \$99,300, and \$126,000 for 1200, 2300, and 3200 ft² plants.

Canned rotor pumps and instrumentation were assumed to be 10-year items. Instruments were grouped as directly associated with control and monitoring of the calcination vessel, health physics and process instrumentation. Yearly costs were \$26,500, \$46,200, and \$57,900 for the three hypothetical plants.

Total capital costs per year as a function of plant size and shielding wall thickness range from \$163,000 for a 1200-ft² plant with 4-ft canyon walls to \$365,000 for a 3200-ft² plant with 7-ft walls (Fig. 4.2). This corresponds to a range of 1.2×10^{-3} to 2.8×10^{-3} mill/kwh_e for calcination capital costs. Calcination operating costs are to be calculated next.

5.0 DISPOSAL IN DEEP WELLS

5.1 Disposal by Hydraulic Fracturing (W. de Laguna)

Two ORNL drilling crews, with the help of two crews from the Corps of Engineers, have completed 15 test holes in the area of the second fracturing experiment. Partial analysis of the results of this work show that the geologic structure in this area is more complex than anticipated and that folds or faults in the shale have influenced the shape of the grout sheet. It may be necessary to suspend the drilling operations shortly in order to make a detailed study of the work completed as a guide to further drilling. Nothing that has been found is unfavorable to the potential use of the method, but the shape of the grout sheet is not that anticipated.

A contract has been let for a 3000-ft core hole to determine the possibility of injecting waste into the lower part of the Rome formation, which is not exposed at the surface. Since it now appears that the structure of the beds is important, the need for a seismic survey of the area of the second experiment and of the proposed site for the operating plant is being investigated.

Several major petroleum companies and oil-field service companies have been invited to submit proposals for research and development of possible waste-clay-

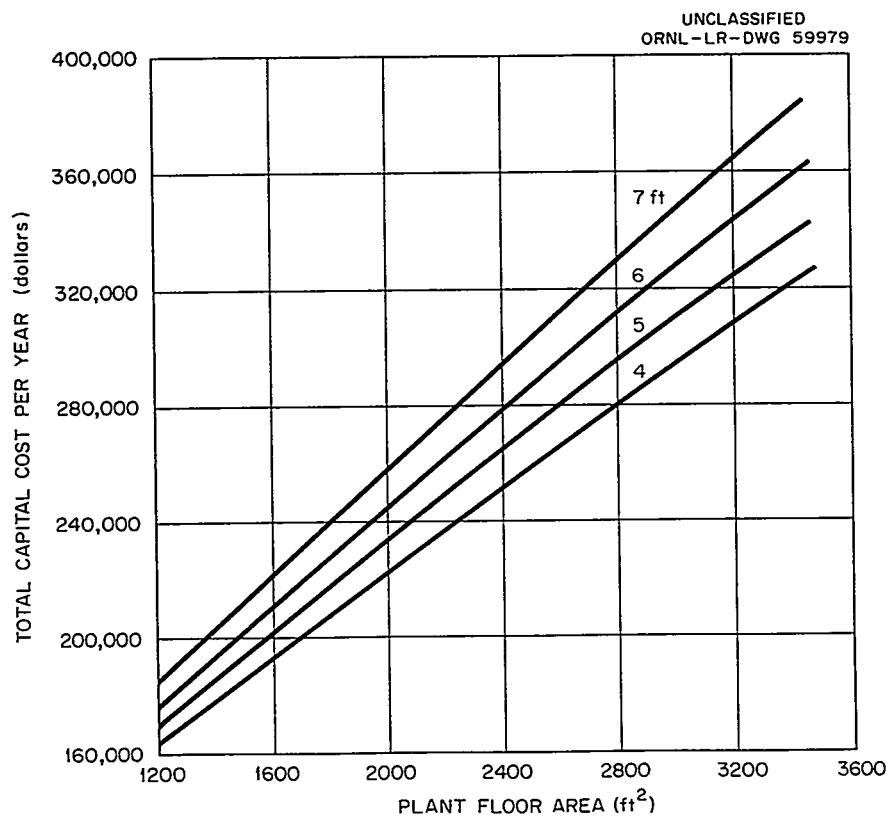


Fig. 4.2. Total Capital Costs per Year as a Function of Plant Floor Area and Shielding Wall Thickness.

Table 4.3 Process Equipment Costs

Item	Cost		
	1200-ft ² Plant	2300-ft ² Plant	3200-ft ² Plant
20-year amortized items			
Feed and off-gas equipment	\$ 70,000	\$ 70,000	\$ 70,000
Furnaces	70,000	170,000	230,000
Manipulators with hoists	160,000	240,000	320,000
Remote welding equipment	15,000	15,000	15,000
Pipe, valves, fittings, etc.	110,000	180,000	220,000
Electrical	30,000	50,000	65,000
Insulation	15,000	25,000	35,000
Sampling	20,000	20,000	20,000
Subtotal	490,000	770,000	975,000
Construction overhead	200,000	310,000	390,000
Engineering	75,000	115,000	150,000
Contingency	100,000	155,000	200,000
Total	\$ 865,000	\$ 1,350,000	\$ 1,715,000
Cost per year (4% interest)	\$ 63,700	\$ 99,300	\$ 126,000
10-year amortized items			
Canned rotor pumps	\$ 6,000	\$ 14,000	\$ 19,000
Instrumentation			
Pot line	60,000	140,000	190,000
Process	35,000	35,000	35,000
Health physics	20,000	20,000	20,000
Subtotal	120,000	210,000	265,000
Construction overhead	50,000	85,000	110,000
Engineering	20,000	35,000	40,000
Contingency	25,000	45,000	55,000
Total	\$ 215,000	\$ 375,000	\$ 470,000
Cost per year (4% interest)	\$ 26,500	\$ 46,200	\$ 57,900

cement mixtures and for engineering consultations in the design of the proposed ORNL Fracturing Disposal Plant.

6.0 DISPOSAL IN NATURAL SALT FORMATIONS

6.1 Field Tests (F. M. Empson)

A complete description of startup and operation of the large field experiments was given previously (19), and accumulated operating data from the large experiments, together with data from associated experiments in both the laboratory and the field have been reported (20).

The average waste temperature in both acid and neutralized waste was quite sensitive to abrupt power failures, but dropped very slowly with the reductions in power simulating fission product decay (Fig. 6.1). The acid-waste cavity showed a continuing slight temperature decrease after 100 days' cooling. The neutralized-waste cavity was still in operation during cooling of the acid waste and may have affected the cooling rate. Average temperature for the neutralized-waste cavity reached a maximum 10°C higher than the acid cavity. Irregularities in the plotted points for the neutralized-waste cavity early in the experiment are due to temperature variations in the sludge.

The acid-waste experiment was terminated after 197 days' operation and the neutralized-waste experiment after 392 days. In each case, temperatures were allowed to fall naturally until the waste and the surrounding salt temperatures returned to ambient, i.e., ~100 days. After the solutions reached ambient temperature, the acid waste was pumped from the cavity into polyethylene carboys and then the neutralized into steel drums and removed from the mine. These cold waste solutions were processed through the industrial waste treatment facilities of a government-owned aircraft plant (operated by the Boeing Airplane Company at Wichita, Kansas) designed to handle plating and similar industrial wastes.

Investigation of the conditions in the two experimental cavities is now underway, including detailed measurements of the cavities for comparison with those made before the experiments. Samples of recrystallized salt and other materials in the emptied cavities will be returned to ORNL for analysis.

In the acid-waste cavity there is little undercutting at the liquid level. The surfaces of the cavity walls below the liquid level are pitted with pockets 4-6 in. deep. Most of the damage seems to have occurred below the liquid level. Salt is deposited on the bottom to a depth of about 1 ft.

In the neutralized-waste cavity there is a deep (~16 in.) undercut of the shale parting at the elevation of the vapor-liquid interface. The walls are covered with a

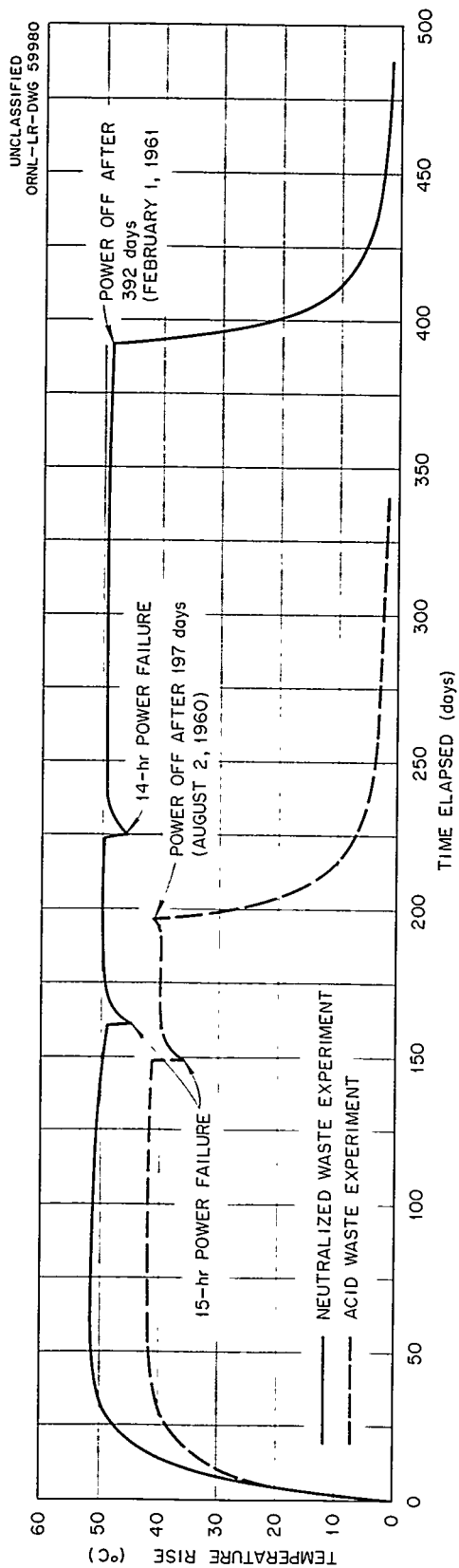


Fig. 6.1. Average Temperature Rise in Waste.

heavy layer of recrystallized salt, and a layer of recrystallized salt also covers the sludge at the bottom, and a shelf of recrystallized salt extends 12-15 in. out from the wall just above the liquid level.

Contract arrangements with the Carey Salt Company call for removal of experimental equipment from the mine. The equipment was dismantled as various operations were completed and is now essentially finished. One power supply has been kept in operation to supply power to small experiments still in operation. All pumps, tanks, electrical equipment, gas cleaning equipment, and instruments have been packed for shipment to ORNL.

6.2 Plastic-Flow Studies (W. J. Boegly, Jr.)

When an opening is mined in an underground formation, the stresses produced by the overburden pressure are disturbed, resulting in a process of stress redistribution within the formation. The pattern and magnitude of the stress concentrations are dependent on the structural properties of the material, the percentage extraction, the shape of the opening, and the depth.

In salt mining, the volume of salt removed can produce stresses in the pillars greater than the elastic limit, and plastic flow will result. Plastic flow produces a change in room dimensions, thereby reducing the stresses in the salt surrounding the room and resulting in a new condition of stability. The size of the plastic zone increases with rising temperature, resulting in an increased plastic flow (creep rate). Some plastic flow measurements in salt mines have been reported by Reynolds and Gloyne (21) and Busch (22), but sufficient data are not available to predict the rate and extent of the flow to be expected in any mining situation. The empirical equations that have been developed apply only to a specific mine.

Laboratory determinations of the physical properties of rock salt and the effect of temperature and gamma radiation on these properties have been reported by Gunter and Parker (23). As expected, increased temperature produced an increase in creep rate and a decrease in the compressive strength and the modulus of elasticity. Gamma irradiation to 5×10^8 r produced little change in the structural properties, although there was an indication that some decrease in compressive strength occurred at the higher doses. These studies will be extended to gamma doses greater than 5×10^8 r with samples of salt from various mines.

Gages were installed in the Carey Mine to measure plastic flow in the vicinity of the large cavities (Fig. 6.2). Two types of gages were installed: extensometers, to measure the linear movement of salt between two reference points, and strain seismographs, to determine if movement occurred with a constant or variable velocity. Measurements were made of the floor-to-ceiling movement, column-to-column movement, and floor movement. A special gage, called the "Reidometer", was installed after the experiments were underway to determine what portion of the total

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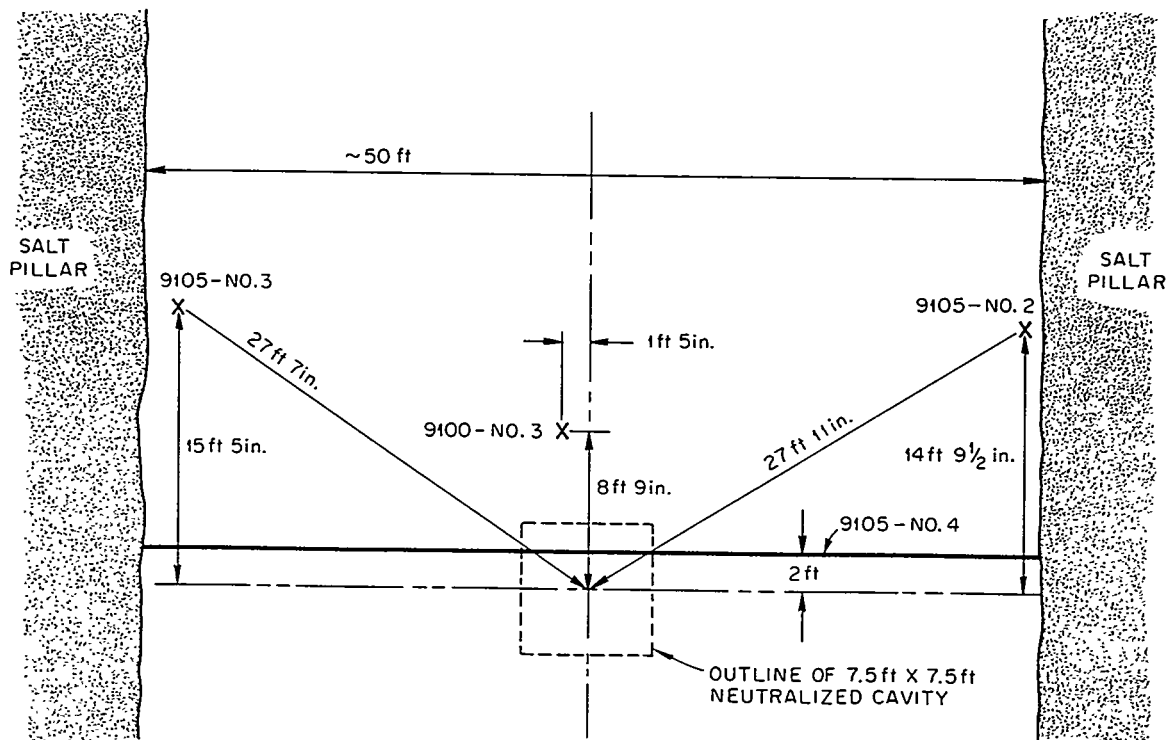


Fig. 6.2. Location of Extensometers Around Neutralized-Waste Cavity.

floor-to-ceiling movement, indicated by the extensometers, was actually floor movement.

The gages were installed after the cavities were excavated, and readings were taken for 110 days prior to startup. The rate of movement observed during this period was almost constant for each gage (Table 6.1). The gages near the columns (9105, Nos. 2 and 3) showed a rate of movement about 50% of the movement in the center of the room (9100, No. 3). Although the total column-to-column movement was equal to approximately half the floor-to-ceiling movement in the center of the room, the change in length per unit length (unit deformation) was much less, only about 13% of the unit deformation in the center of the room.

When heat was applied to the cavity at startup, the rate of movement increased rapidly due to increased creep and thermal expansion of the salt (Fig. 6.3). With time, this apparent increased rate of movement slowly decreased until, at constant temperature, the rate was approximately equal to that observed prior to heating. After the heaters were turned off, the salt actually contracted, causing an increase in room dimensions. This effect is now disappearing. The latest gage readings indicate that, although the total movement was greater than normal, these heated cavities did not significantly upset the rate of movement or the stability of the experimental room.

At ~500 days after installation the gage measuring column-to-column movement started to show an unexpected increase in rate of movement, from 0.0003 in./day to ~0.0005 in./day. During disassembly of test equipment, it was discovered that two of the wires that supported the gage from the ceiling were broken. This may account for the apparent increase in movement of about 0.03 in. in the last 125 days (Fig. 6.3). The column-to-column curve will be analyzed further to verify this.

Floor movement in the area surrounding the neutralized-waste cavity is toward the cavity. Due to difficulties in attaching the gages to the salt without disturbing the mine floor, the data are not consistent from gage to gage. However, the gages did show that the salt was forced back away from the cavity when the waste was added, but that the flow reversed its direction when heat was applied.

Preliminary analysis of the strain seismograph charts indicates that the salt is moving with a constant velocity. A more detailed analysis of these records is in progress to definitely establish that no unusual movement occurred during the rapid expansion of the salt at the start of the experiments.

6.3 Thermal Studies (R. L. Bradshaw)

In salt disposal of high-level radioactive wastes it is necessary to predict as accurately as possible the waste temperature rise that will occur due to the heat

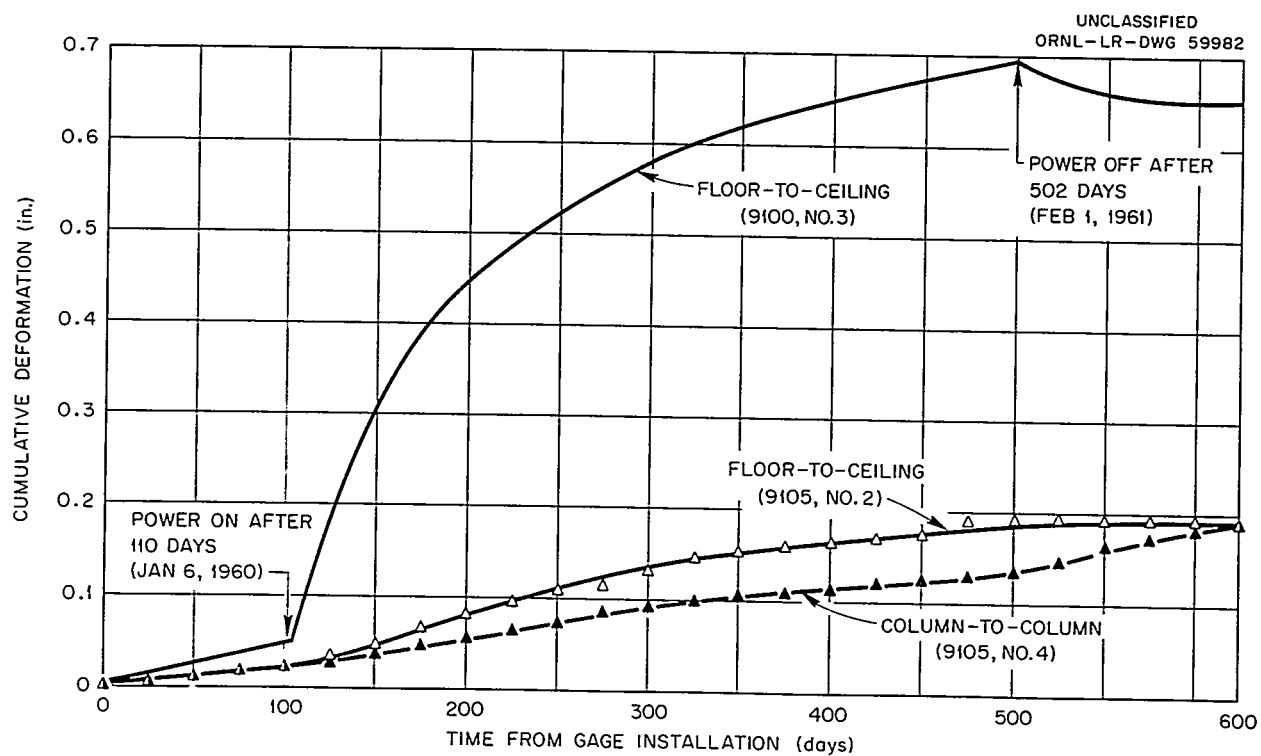


Fig. 6.3. Total Deformation for Various Gage Locations Around Neutralized-Waste Cavity.

Table 6.1 Average Extensometer Results for 110 Days Prior to Heating

Gage	Gage Length (in.)	Total Movement (in.)	Average Rate of Movement (in./in./yr)*
9105, No. 2	157.5	0.0239	5.0×10^{-4}
9105, No. 3	162.8	0.0266	5.4×10^{-4}
9105, No. 4	602	0.0253	1.4×10^{-4}
9100, No. 3	153.7	0.0512	11.0×10^{-4}

* Creep rate, based on straight-line fit of data during period.

generated by fission product decay. The allowable rise will be limited by the boiling point for liquid wastes and by the decomposition temperature for solid wastes. A further limit on temperature rise may be imposed by the effects of increased temperature on the structural properties of salt.

The temperature rise in a mine disposal operation will be a function of the irradiation and decay history of the waste, the thermal properties of the waste and of salt, the waste cavity size and shape, and the spacing between cavities.

Solutions for the steady-state temperature rise with a constant heat generation rate are available for a number of simple geometries, such as the slab or the sphere, but, for transient temperatures with heat sources that are decaying at a nonuniform rate, solutions are either nonexistent or require computer calculation.

The first thermal studies (computer calculations) in connection with disposal in salt dealt with the temperature rises in spheres of various diameters containing liquid wastes from fuel which had been irradiated to 10,000 Mwd/ton and which produced 800 gal of waste per ton. These studies indicated that it would be possible to store 2-year-cooled waste in a sphere of 10 ft dia without exceeding the boiling point.

The two 7.5-ft-cube field cavity experiments (Sect. 6.1) were designed to check the sphere calculations, the surface area of the cube being approximately the same as that of a 10-ft sphere. Sphere calculations, assuming complete mixing of the waste, predicted a maximum temperature rise of 50°C. In the acid-waste cavity, where convective mixing was good, the maximum average waste temperature rise was 42°C. In the neutralized-waste cavity, which contained a viscous sludge, the maximum average temperature rise was 52°C. Temperature rises out in the salt formation were also in good agreement with the theoretical calculations.

The field experiments thus lent confidence to the theoretical calculations, at least for cases in which the salt temperature rise is only a few degrees above ambient. However, laboratory tests of the thermal properties of pure salt crystals indicate that these properties change rapidly with temperature, viz. by a factor of 2 between 0 and 200°C, and, since the theoretical calculations are based on the laboratory values, field tests should be made to ascertain if the thermal properties of natural salt in situ behave similarly. Such tests are planned during the next fiscal year.

An actual disposal operation will consist of a number of waste cavities spaced as closely as possible without exceeding the allowable temperature rise. If it is assumed that the disposal operation is handling the output from a fuel processing plant serving the entire U. S. power reactor economy ca. 1970, wastes would be coming in at a rate such that it would be reasonable to assume that the heat source is a slab of infinite horizontal dimensions. Preliminary approximate calculations, which assume that the waste is uniformly distributed in the slab, indicate that, for 8-year-cooled wastes from the hypothetical plant, a gross mine area of about 10 acres per year would be required.

A new computer slab-source code has been developed which will allow a more accurate calculation to be made covering a wider range of irradiation histories and cooling times. In addition, this code will evaluate temperatures out in the salt as well as in the slab itself so that the effects of finite vertical dimensions of salt deposits may be investigated. This code is now undergoing "debugging."

Since the slab calculation assumes that the heat source is uniformly distributed, it becomes necessary to make a correction for discrete sources. Initially it is planned that a study be made of the time-space-temperature distribution around cylinders of various length/diameter ratios since cylinders are a likely storage geometry. The solutions for the cylinder and the slab can then be merged so that, for any given cylinder dimension and maximum allowable waste or salt temperature rise, the required spacing between cylinders may be calculated.

6.4 Salt Cavity Alterations (H. Kubota*)

Considerable alteration in the shape of test cavities has been observed, both in laboratory experiments with salt blocks and in the field experiments conducted in the Carey Salt Company's Hutchinson mine. Maximum erosion into the salt wall usually occurs at the liquid level. Deposits of salt are formed on the liquid surface, on any object that extends down into the liquid, and on the walls. Additional re-crystallized salt is sometimes deposited at the bottom of the cavities.

A laboratory program was initiated to resolve the factors responsible for this cavity deformation. In order to facilitate observation, a series of cylindrical blocks of salt was used, partially immersed in liquid and contained in a closed vessel. Salt cylinders 2.25 in. dia, which were core-drilled at the Hutchinson

* Analytical Chemistry Division, ORNL.

mine, were cut into 6-in.-long sections for this purpose. Glass containers with tightly fitting covers were used.

6.4.1 Measurements at 25°C

As a first approach, studies were made with salt blocks in various solutions at 25°C, at which temperature it is relatively easy to maintain isothermal equilibrium between solid, liquid, and vapor phases. This condition is desirable in approaching the equilibrium exchange of water between liquid and vapor phases. The results indicate that a salt cavity in an isothermal system at 25°C will resist attack by an aqueous solution as long as the solution is saturated with salt and, that the presence of other ions does not affect the integrity of the salt cavity.

In the experiments the salt block was weighed and placed upright in a glass container with the long axis vertical. Four solutions were used in the containers: (I) water, (II) saturated sodium chloride, (III) saturated sodium chloride and sodium nitrate, and (IV) saturated sodium chloride-5 M hydrochloric acid. Solution III contained an anion whose sodium salt is more soluble than sodium chloride, while solution IV contained the hydronium cation, whose compound with chloride is more soluble than sodium chloride. Where solutions were salt saturated, 10 g of sodium chloride (analytical grade, fine crystals) was placed at the bottom of the bottle. In each test 100 ml of the solution was carefully poured in so that the salt block was not wet at any point above the final liquid level. The bottle was sealed and immersed in a water bath maintained at 25°C.

The time of immersion was 27 days. No special significance is attached to this time, but all subsequent tests were conducted over the same time span. At the end of the time the blocks were removed, wiped free of adhering liquid, air dried for 24 hr, and weighed (Fig. 6.4). The density of each solution was measured before and after the test (Table 6.2).

Water (I) was the only medium in which any noticeable change took place. The diameter of the immersed portion of the salt cylinder was reduced uniformly to 2-3/16 in. except at the water line, where it was 2 in. The excessive erosion at the water line was due to surface motion of the liquid imparted by the thermostat stirrer. The 35-g weight loss approximates the solubility of sodium chloride in water at 25°C (35.9). Neither measurements with a pair of calipers nor weight loss showed changes in the blocks in the other three media.

6.4.2 Measurements at 75°C

A salt block was partially immersed in a saturated salt solution maintained at 75°C. Since only the solution was heated, the vapor phase was cooler than the liquid and a large amount of vapor condensed and dropped directly into the liquid or flowed down the sides of the bottle into the liquid (Fig. 6.5a). The salt was eroded just at the water

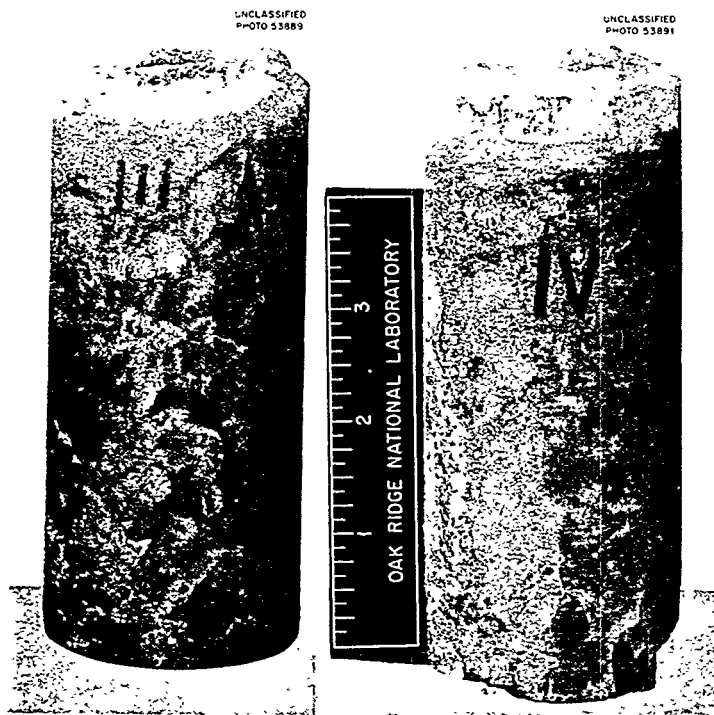
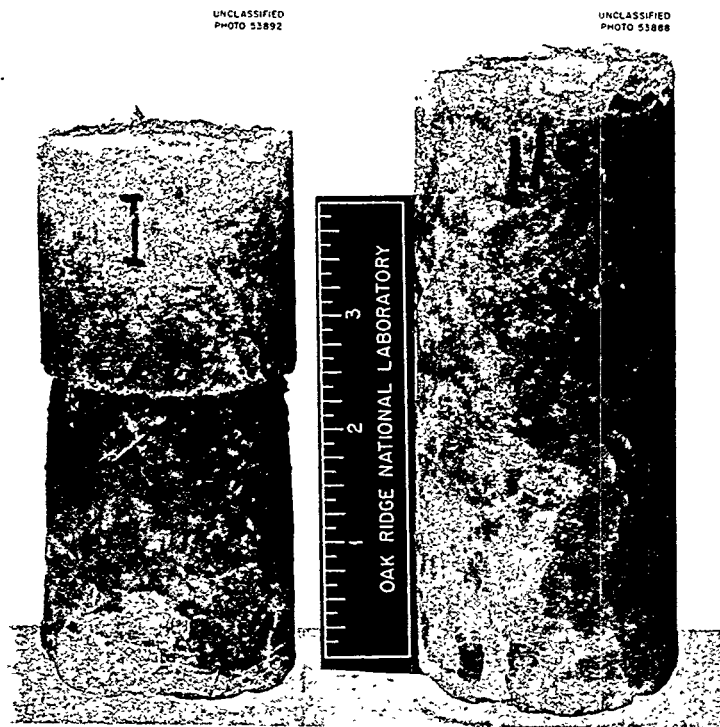
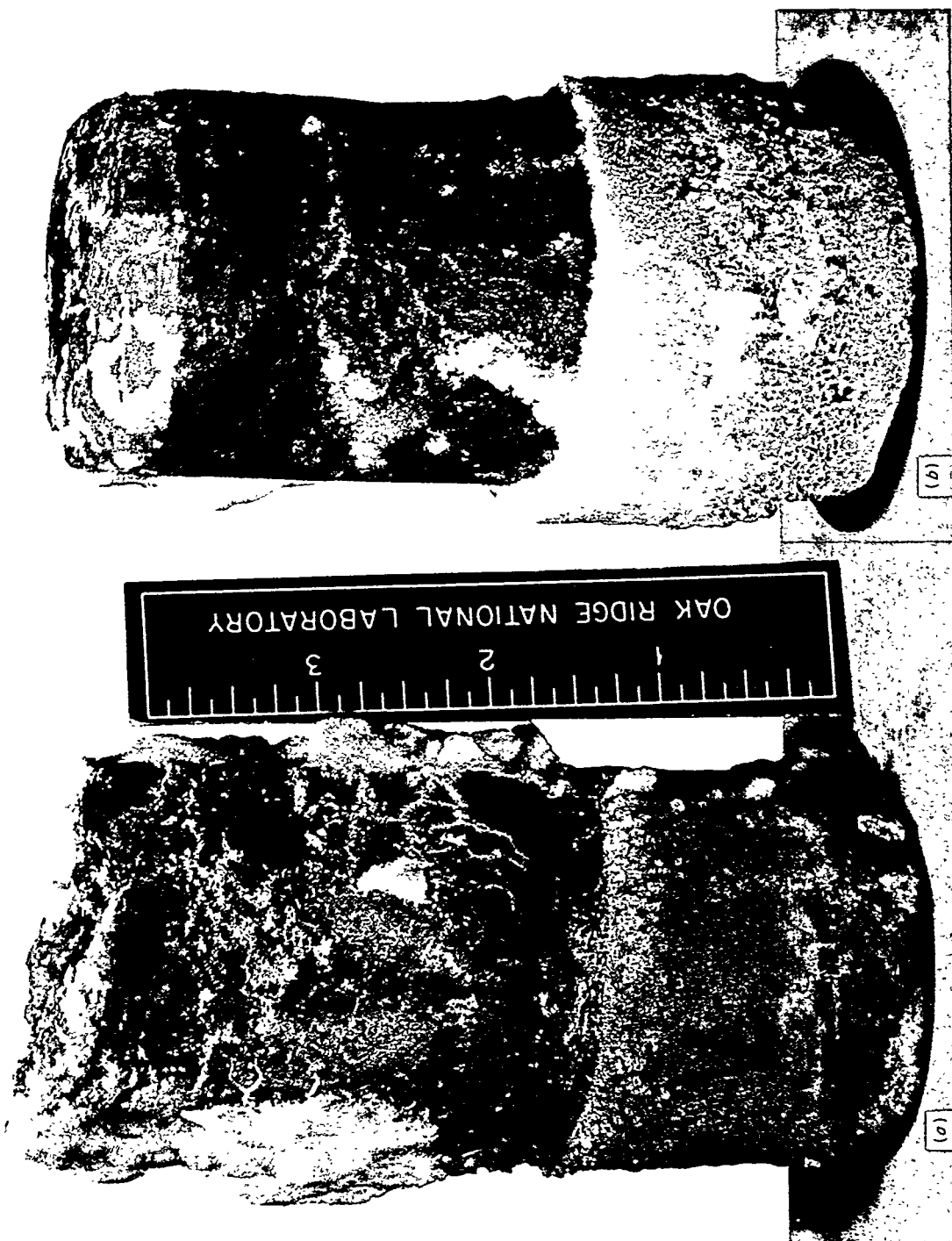


Fig. 6.4. Erosion of Salt Blocks at 25°C in 27 days in (I) Distilled Water; (II) Saturated NaCl Solution; (III) Saturated NaCl-NaNO₃ Solution; (IV) Saturated NaCl-5 M HCl Solution.

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Fig. 6.5. Erosion of Salt Block in Saturated NaCl Solution at 75°C. (a) No Collar;
(b) Protecting Collar Around Block.

Table 6.2 Erosion of Salt Blocks at 25°C in 27 days

Solution	Weight of Block, g		Loss, g	Density of Medium, g/cm ³	
	Before	After		Before	After
(I) Water	665	630	35	0.998	1.194
(II) Saturated NaCl	762	762	0	1.193	1.194
(III) Saturated NaCl and NaNO ₃	703	704	-1	1.333	1.333
(IV) Saturated NaCl and 5 M HCl	735	735	0	1.116	1.116

line, and recrystallized salt was deposited on the block below the liquid level and in the vapor area.

It can be postulated that the loss of a finite amount of water vapor will cause oversaturation in the liquid. Therefore salt selectively crystallizes out on the salt wall. When condensate in the vapor phase, which contains very little solute, returns to the surface of the liquid, there is unsaturation just at the surface, which produces erosion at the water line.

To test this hypothesis, a salt block was encased in a glass collar 2.5 in. dia extending 0.5 in. above the surface. A funnel was inverted over the block in the vapor area so that condensate from the vapor would drop back into the solution outside the collar, with no contact between the unsaturated solution and the salt block. The solution outside the collar returned to saturation by dissolving some of the salt placed at the bottom of the container. No erosion was seen at the water line (Fig. 6.5b), but the deposit of salt below the liquid level was more pronounced. There was some dissolution of the salt in the vapor phase, attributed to dissolution of salt by water vapor, which was not observed at 25°C because of the low vapor pressure of water at that temperature.

The study of cavity alterations, thus far, indicates that when the liquid phase is heated, to simulate heat distribution in a high-level liquid waste, finite changes occur in salt concentration. When the solution is temporarily oversaturated, due to vaporization of water, recrystallized salt is deposited on the cavity walls and bottom. In one zone of unsaturation, at the liquid-vapor interface where unsaturated condensate re-enters the liquid, salt dissolves until the solution returns to a saturated state. Water vapor is a second zone of unsaturation, and salt in contact with the vapor is slowly dissolved. At higher temperatures and, consequently, higher vapor pressures, the salt dissolution by the vapor increases in rate.

7.0 CLINCH RIVER STUDY

7.1 Estimate of Activity in Bottom Sediments (L. Hemphill, P. H. Carrigan,* W. B. Nix)

A basic aim of the Clinch River Study is to determine the fate of radioactive materials released to the river channel. The results of annual Applied Health Physics bottom sediment sampling, conducted since 1951, indicate that a significant fraction of the radioactivity released by ORNL is deposited in the river bed.

A special sampling of the Clinch River bottom sediments has been conducted in conjunction with the Applied Health Physics Section. In general, the two groups sampled the same river cross-sections; however, additional cross-sections were sampled by the Clinch River Study Group of the Waste Disposal Research Section in order to provide better development of the longitudinal distribution of radioactivity. Also, core samples of the bottom sediments, rather than the Eckman dredge samples taken by the Applied Health Physics Section, were obtained in order to provide information on the vertical distribution of radioactivity.

7.1.1 Methods

Core samples were taken at eight to ten equally spaced intervals within each cross-section. Core collection consisted of plunging a 3/4-in. i.d. x 14-in.-long plastic tube, contained in a weighted stainless steel tube, into the sediment. Immediately after sample withdrawal, the plastic tube was sealed with rubber stoppers.

The samples were prepared for radiochemical analyses according to the following procedure: (1) Each core was frozen in its plastic tube, (2) extruded from the tube, (3) sliced into 1-in.-long x 3/4-in.-dia cylindrical segments on a cutting block, (4) transferred to a labeled test tube, (5) weighed and stoppered. The gross gamma activity of the 1-in. sample was measured with a gamma scintillation detector and scaler. Each sample and control (background sample) were counted for a 10-min interval.

Examination of the initial gross gamma counts indicated that many of the 1-in. segments were too low in activity to attempt individual radiochemical or gamma spectrometric analysis. Because of the low concentration of radionuclides in many segments, all segments from a cross-section were mixed to form a homogeneous composite sample. The composited samples were dried at 100°C, sealed in 3-in. dia x 1.5-in.-high plastic containers, and counted in a 256 gamma spectrometer. The Sr-90 activity of each composite sample was determined by radiochemical separation and beta counting.

7.1.2 Results

Data collected during core-sampling operations, i.e., section width, water depth, and sediment depth, were incorporated into scale drawings of each river cross-section.

*On loan from Tennessee District, Surface Water Branch, Water Resources Division, U. S. Geological Survey.

The cross-sectional area and the sediment volume of the 17.8-mile reach of the river below White Oak Creek were calculated by point-to-point numerical integration (Table 7.1).

Table 7.1 Clinch River Cross-Sections

Total silt volume: 491 acre-ft

Location (CRM)	Width at Water Surface (ft)	Cross-Sectional Silt Area* (ft ²)	Cross-Sectional Area* (ft ²)	Average Silt Density** (g/cm ³)
4.7	600	325	16,350	1.4339
5.8	670	375	13,525	1.3210
6.9	800	473	15,025	1.4813
8.0	705	419	14,225	1.3596
9.0	525	318	14,975	1.3139
10.0	1,050	581	13,650	1.4450
11.0	630	375	10,795	1.1731
12.0	480	143	11,655	1.3079
13.0	430	267	8,644	1.2430
14.0	500	192	8,725	1.2913
14.6	400	114	7,275	1.3448
15.3	420	113	7,797	1.3650
16.0	660	307	8,310	1.5161
16.9	350	58.7	6,115	1.2210
18.1	365	73.3	6,090	1.4887
19.5	350	50.0	5,730	1.2361
20.8	400	49.6	4,773	1.4024
21.6	370	113	3,630	1.3833
22.5	400	----	4,490	1.1660

* Calculated from field measurements collected during core sampling.

** Wet weight sample.

It can be seen in Table 7.1 that the river channel changes in shape and width around CRM 16.9. Upstream from this cross-section, the channel is relatively narrow and shallow, with nearly vertical banks. The shallow sediment deposits in this reach are very close to the banks. By comparison, the cross-sections downstream from CRM 16.9 are wider and shallower along the banks. The sediment deposits in this reach are deep and generally continuous across the entire channel width. The relative gross gamma activity at each cross-section was estimated by substituting the corrected counting rates in a point-by-point area and mass integration calculation (Tables 7.2 and 7.3).

The shapes of the curves of the "Flounder" readings and the gross gamma activity of sediment cores, both sets of data plotted with reference to maximum "Flounder" readings at CRM 11.0, are similar (Fig. 7.1), but there are obvious areas of disagreement about CRM's 20.8, 16.9, 14.0, 10.0, 9.0, and 8.0. To a large extent, this disagreement is most pronounced in areas where sampling cross-sections did not coincide. Disagreement at coincident cross-sections probably arises from the difference in measurement techniques. The "Flounder" detects the activity in a relatively large volume near the top of the sediment. In contrast, the core data are essentially a number of measurements of weighted point sources averaged over the whole cross-section.

Gross gamma measurements of the 1-in. core samples showed no uniform vertical distribution pattern. In general, activity decreased with depth, but the rate of decrease was too irregular to define the lowest stratum of activity in the sediment.

Measurable amounts of Cs-137, Ru-106, and Co-60 were present in all composited samples. Spectrometric data were compared with standard soil samples containing known amounts of the nuclides to determine the absolute activities of each sample. Each datum was transformed to activity per mile of river (Table 7.4, Fig. 7.2a,b,c,d) by the following calculation:

Let $N(X)$ = average specific activity ($\mu\text{c}/\text{kg}$) of the silt at CRM X;

$\rho(X)$ = average silt density (g/cm^3)

$A_s(X)$ = silt cross-section (ft^2)

at the same point. One can write

$$\begin{aligned} \frac{dc}{dX}(X) &= \text{number of curies per mile of river} \\ &= N(X) [\mu\text{c}/\text{kg}] \times 10^{-6} \text{ curie}/\mu\text{c} \times 10^{-3} \text{ kg}/\text{g} \times \rho(X) [\text{g}/\text{cm}^3] \\ &\quad \times (30.5 \text{ cm}/\text{ft})^3 \times A_s(X) [\text{ft}^2] \times 5280 \text{ ft}/\text{mi} \\ &= 0.1498 N(X) \rho(X) A_s(X) \end{aligned}$$

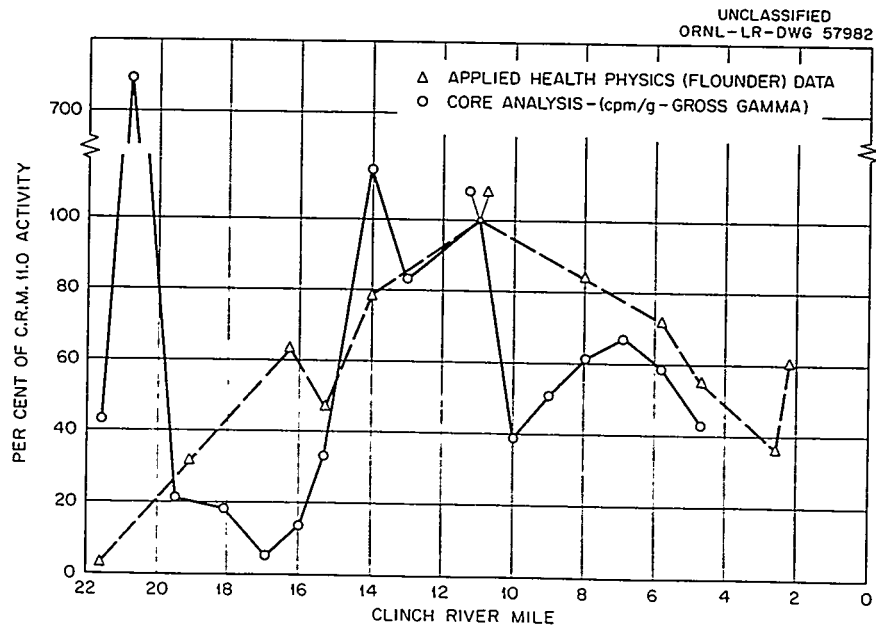


Fig. 7.1. Comparison of Core Data (Gross Gamma) and "Flounder" Data.

Table 7.2 Sample Calculations of Gross Gamma Activity
in CRM 11.0 Section

Distance from Initial Point (ft)	Width (ft)	Depth (ft)	Mean Core Depth (ft)	Sediment Area (ft ²)	Gross Gamma Count per Total Core Depth (10 ³ cpm/ft)	Mean Gross Gamma Count (10 ³ cpm/ft)	Total Gamma Count (10 ⁶ cpm)
0 LB	0	0	0	0	0	0	0
50	50	0.750	0.375	10.4	87.4	43.7	2.18
150	100	0.417	0.583	58.3	73.4	80.4	8.04
250	100	0.667	0.542	54.1	153	113	11.30
350	100	0.917	0.792	79.2	135	144	14.39
450	100	0.667	0.792	79.2	160	148	14.77
550	100	0.667	0.667	66.7	145	153	15.26
630 RB	80	0	0.333	26.7	0	72.5	5.80
				374.6			
							71.74

Specific Activities:

Areal

$$K_A = \frac{71.7 \times 10^6 \text{ cpm}}{375 \text{ ft}^2} = 191 \times 10^3 \frac{\text{cpm}}{\text{ft}^2}$$

Gravimetric

$$K_g = \frac{71.7 \times 10^6 \text{ cpm}}{4.7 \times 10^5 \text{ g}} = 152 \text{ cpm/g}$$

Equation:

$$K_A = \int c \left(\frac{\text{cpm}}{\text{ft}^2} \right) dA (\text{ft}^2) \approx \sum c \left(\frac{\text{cpm}}{\text{ft}^2} \right) \Delta W (\text{ft}) \sum y (\text{ft}) =$$

$$= \sum \left[c \Delta y \left(\frac{\text{cpm}}{\text{ft}} \right) \right] \Delta W (\text{ft}), \Delta y = \text{constant}$$

Table 7.3. Distribution of Gross Gamma Activity
In Clinch River Bottom Sediment from Mile 21.6 to 4.7.

Cross-Section Location (CRM)	1959 - Applied H.P. "Flounder" Data* (cpm)	1960 - Clinch River Study Core Analysis Data (activity, cpm/g)
2.1	9,120	
2.6	5,460	
4.7	8,280	66.1
5.8	10,860	89.2
6.9		102
8.0	12,780	92.5
9.0		78.0
10.0		59.7
11.0	15,180	152
12.0		103
13.0		127
14.0	11,800	173
14.6		4.1
15.2	7,080	
15.3		50.6
16.0		20.9
16.3	9,540	
16.9		7.2
18.1		27.9
19.1	4,860	
19.5		32.0
20.8		
21.5	360	1,080
21.6		66.3
27.5	240	

* From reference 24.

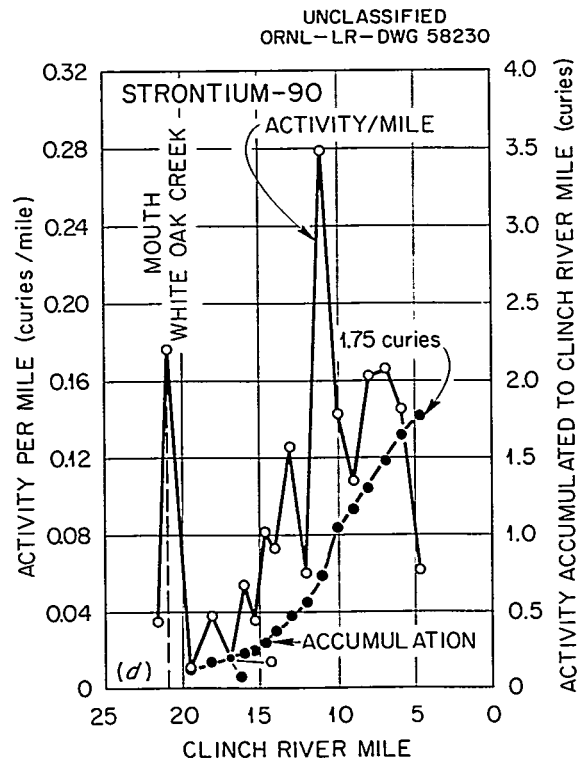
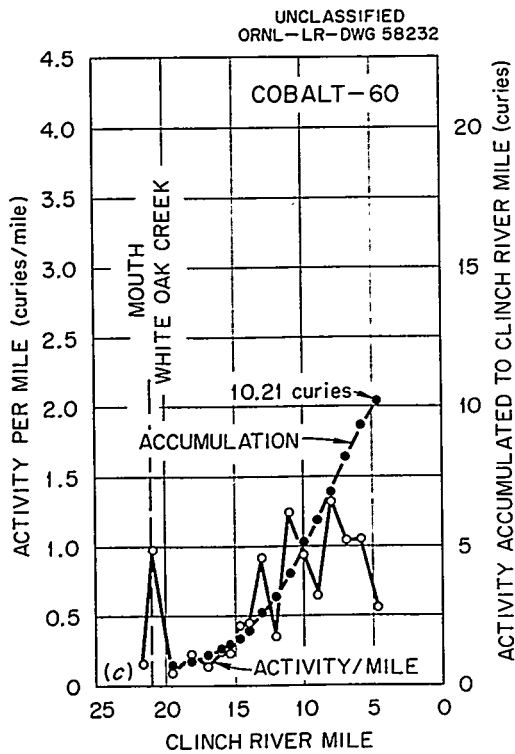
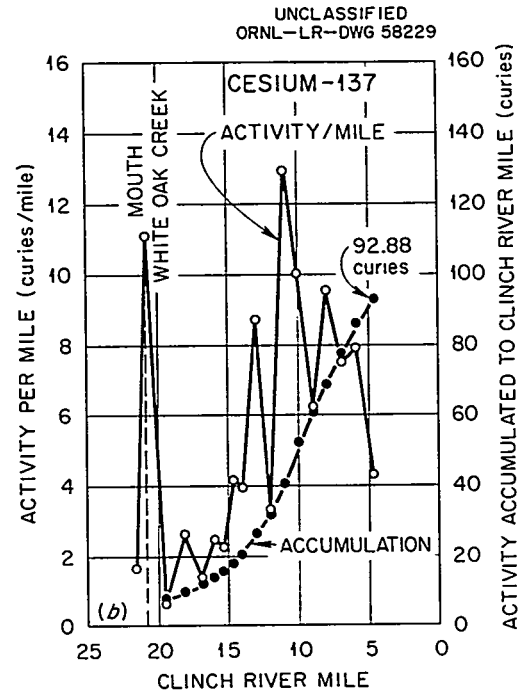
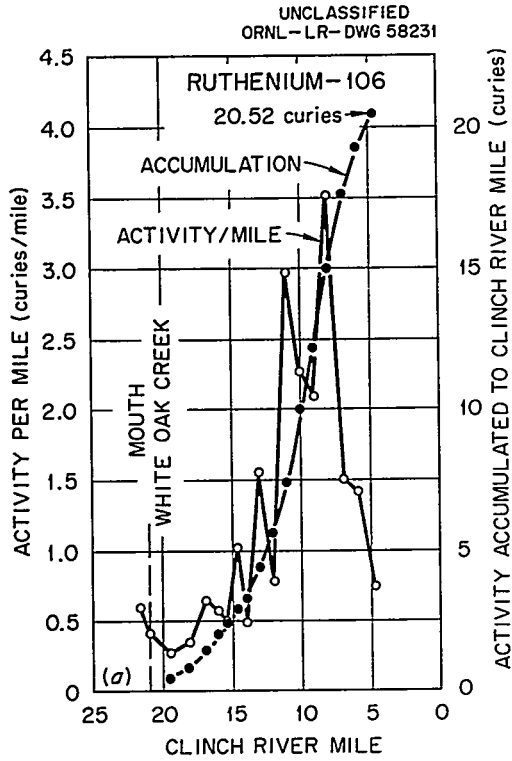


Fig. 7.2. Ru^{106} Activity per Mile in Clinch River due to Ru^{106} , Cs^{137} , Sr^{90} , and Co^{60} .

Table 7.4. Analysis of Clinch River Silt for Specific Radionuclides*

Clinch River Mile	Ru ¹⁰⁶ Activity		Cs ¹³⁷ Activity		Co ⁶⁰ Activity		Sr ⁹⁰ Activity	
	Specific (10 ⁻² µc/kg)	Per Mile (curies/mile)	Specific (10 ⁻¹ µc/kg)	Per Mile (curies/mile)	Specific (10 ⁻² µc/kg)	Per Mile (curies/mile)	Specific (10 ⁻² µc/kg)	Per Mile (curies/mile)
4.7	1.05	0.734	0.622	4.33	0.788	0.549	0.856	0.060
5.8	1.91	1.41	1.06	7.87	1.42	1.05	1.94	0.144
6.9	1.43	1.50	0.721	7.55	0.995	1.04	1.58	0.165
8.0	4.13	3.52	1.12	9.51	1.55	1.32	1.89	0.161
9.0	3.34	2.09	0.995	6.22	1.03	0.644	1.71	0.107
10.0	1.81	2.27	0.797	10.02	0.752	0.944	1.13	0.141
11.0	4.50	2.96	1.97	12.96	1.89	1.24	4.23	0.278
12.0	2.81	0.783	1.19	3.33	1.24	0.345	2.12	0.059
13.0	3.12	1.55	1.76	8.71	1.84	0.912	2.52	0.125
14.0	1.33	0.492	1.06	3.94	1.19	0.442	1.94	0.072
14.6	4.41	1.01	1.81	4.14	1.85	0.423	3.47	0.080
15.3	2.16	0.497	0.977	2.25	0.977	0.225	1.49	0.034
16.0	0.815	0.568	0.354	2.46	0.347	0.241	0.766	0.053
16.9	5.99	0.642	1.32	1.41	1.22	0.131	1.40	0.015
18.1	2.12	0.346	1.61	2.63	1.29	0.211	2.30	0.037
19.5	2.79	0.258	0.712	0.658	0.923	0.0857	1.08	0.010
20.8	3.90	0.405	10.6	11.05	9.32	0.970	16.8	0.175
21.6	2.54	0.594	0.703	1.64	0.653	0.153	1.44	0.034
22.5	1.36		0.248		0.334		0.090	
**								
Total***	20.52		92.88		10.21		1.75	
Total	20.92		97.96		10.66		1.83	

*Ru¹⁰⁶, Cs¹³⁷, and Co⁶⁰ by gamma spectrometer analysis; Sr⁹⁰ chemically separated before counting.

**Total Activity (curies) between CRM 20.8 and 4.7.

***Total Activity (curies) between CRM 21.6 and 4.7.

Cesium-137 is the predominant nuclide at all sections downstream from CRM 21.6. The linear distribution (curie/mi) of Ru-106, Cs-137, and Co-60 is similar from CRM 16.0 to CRM 4.7. Both Cs-137 and Co-60 show a sharp maximum at CRM 11.0, greater than the CRM 20.8 maximum. Ruthenium-106 also shows a maximum at CRM 11.0. Secondary maxima for Cs-137 at CRM 8.0 and 13.0 are greater than the corresponding secondary maxima for Co-60. Generally, the Ru-106 concentration increased regularly from CRM 19.6 to 8.0 and decreased sharply from CRM 8.0 to 4.7. The Cs-137 and Co-60 distribution also generally decreased beyond CRM 8.0, but not so markedly as the Ru-106. The Ru-106 curve shows an approximately symmetrical increase above and below CRM 19.6.

The downstream distribution of Sr-90 (Table 7.4, Fig.7.2d) is similar to that of Cs-137 and Co-60. The points of maximum activity for the four radionuclides coincide. For Sr-90, the maxima, in order of decreasing magnitude, fall at CRM 11.0, 8.0, and 13.0.

To obtain the number of curies of any nuclide in a given reach of river, one takes the above expression and integrates over that reach:

$$C \text{ (curies)} = 0.1498 \int N(X) (X) A_s (X) dX$$

This calculation was performed numerically, point-by-point, for all four nuclides identified from CRM 20.8 to each cross-section and the activities accumulated to each section. Implicit in these calculations is the assumption that (NA_s) for a river bend lies on a straight line between the values in the neighboring straight reaches. That assumption is probably in error and will affect the estimate of total sediment activity. The magnitude and sign of this error are not known, but the estimate of total activity would be expected to be changed less than an order of magnitude.

Between CRM 20.8 and 4.7, the total amounts are 20.52, 92.88, 10.21, and 1.75 curies of ruthenium, cesium, cobalt, and strontium, respectively, for an overall total of 125.36 curies. Another 6.01 curies (total) is between CRM 21.6 and 20.8. Of the 6 curies, 5.08 is due to Cs-137, the remainder consists of 0.45, 0.40, and 0.08 curie of Co-60, Ru-106, and Sr-90, respectively.

8.0 FUNDAMENTAL STUDIES OF MINERALS

8.1 Na-Treated Vermiculite (T. Tamura)

Several methods have been investigated for improving the capacity of vermiculite to sorb strontium. In addition to improving the exchange capacity for strontium by a substitution of sodium for magnesium ions on the exchange complex, different methods by which sodium can be substituted for the crystal lattice potassium in the biotite portion of the vermiculite (hydrobiotite) have been studied.

In one method, 9 liters of 1 M NaCl solution was passed through a 2-cm-dia column containing 50 g of vermiculite. The material in the column was then divided into four approximately equal segments which were compared with the natural and sodium-saturated vermiculite. The natural vermiculite had an exchange capacity of 65 meq/100 g; the 1st section of the leached vermiculite column had 76 meq/100 g; and the 4th section had 68 meq/100 g (Table 8.1). The improvement in sorption is believed to be due to an increase in the exchange capacity of the material.

An even more effective method for increasing the exchange capacity was to treat the vermiculite with sodium tetraphenylboron. Two treatments increased the exchange capacity to 140 meq/100 g and increased strontium removal to 83% as compared to 55% for sodium-saturated vermiculite. The tests were conducted at pH 9.0. X-ray analyses and potassium determinations showed that lattice expansion resulted from sodium substituting for potassium.

To study the effect of pH on strontium sorption, Na-vermiculite was tested at pH 4 and 9. After 72 hr of contact the pH was adjusted with HNO₃ and NaOH. Increasing the pH was beneficial for strontium removal (Fig. 8.1), and the reaction was reversible, as shown by the change in sorption when the pH was readjusted. The cause of the pH effect may be associated with the nature of clay minerals. Clays are known to have two origins for exchange capacity: negative charges from isomorphous substitution in the lattice and dissociation of hydrogen ions from hydroxyl groups at the edges of the crystal lattice. It may be that the lattice source of exchange changes with change in pH. The degree of dissociation should be a function of pH and, hence, the amount of strontium sorbed would also be a function of pH. The effect is found to be most striking below pH 5. Between pH 5 and 9 differences are small; at pH 11 there is another slight increase.

In addition to these methods for increasing the exchange capacity of vermiculite for strontium, the addition of a solution containing NaCl and NaOH was found beneficial. The solution was made 0.9 M NaCl and 0.1 M NaOH and two separate treatments of ten-fold more Na ions than the capacity of the material were given. The vermiculite was thus sodium-saturated in order to eliminate Mg(OH)₂ precipitation and consequent "clogging" of the exchange sites. The treated vermiculite was washed free of excess chlorides before the sorption tests were run.

The dashed curves represent samples of vermiculite which were treated with NaCl only, using the same total sodium ion concentration. An obvious conclusion from the

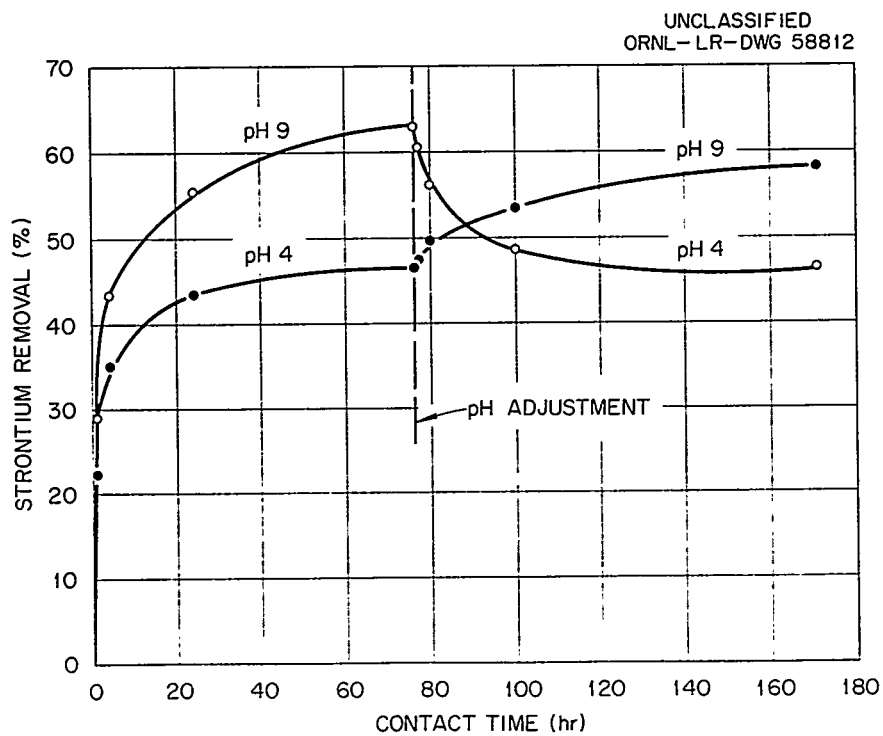


Fig. 8.1. Removal of Strontium by Na-Vermiculite as Related to pH.

Table 8.1 Effect of Sodium Chloride Leaching on Strontium Sorption
Characteristics of Vermiculite

9 liters of 1 M NaCl passed from top of column containing 50 g of vermiculite; tested with 50 ml of 0.1 M NaNO₃ containing 0.05 mg of strontium and 0.5 g of vermiculite

Contact Time (hr)	Sorption (%)					
	Natural Vermiculite	Na-Saturated Vermiculite	NaCl-leached Vermiculite*			
			1st	2nd	3rd	4th
1	3.67	6.91	8.07	7.68	8.49	6.30
4	8.29	16.7	22.7	19.2	16.8	17.6
24	21.5	34.8	46.2	41.6	38.8	35.9
54	24.8	39.6	53.4	48.2	45.2	41.0
120	27.3	41.7	58.0	51.0	48.9	44.8

*1st - 4th refer to the 4 quarters; 1st section is uppermost.

results (Fig. 8.2) is that increasing pH is beneficial for strontium removal as noted earlier. The data also show that the NaCl-NaOH treatment is better than NaCl treatment alone. It is important to remember that the NaCl-NaOH treatment followed NaCl treatment; the latter treatment is necessary to remove the bulk of the magnesium ions from the exchange position and prevent Mg(OH)₂ precipitation when NaCl-NaOH is used.

The cause of the increase by NaCl-NaOH treatment is not yet known. If it is due to ionization of hydrogen ions situated on the edges of the particles, the tests conducted at pH 4.0 should not reflect an increase since ionization can occur only at neutral and alkaline pH. If the treatment causes replacement of lattice potassium by sodium ions, the exchange capacity of the minerals should show an increase. The measurements show that NaCl-NaOH treatment and NaCl treatment do not produce excessive increases; the exchange capacities were 79 and 76 meq/100 g. However, treatment did increase the capacity from 65 meq/100 g.

8.2 Soil Columns (D. G. Jacobs)

Early studies of sorption of cesium by Conasauga shale showed that sorption of cesium by illitic type clay minerals (i.e., those 2:1 layer lattice clay minerals having a nonexpanding crystal lattice) was seriously inhibited by cations having steric favorableness for "edge fixation" sites. Thus potassium, rubidium, and ammonium ions normally inhibit the sorption of radiocesium to a marked degree, as cesium is generally removed from solution by "edge fixation" by the illitic type clay minerals or by simple ion exchange in the freely expanding clay minerals.

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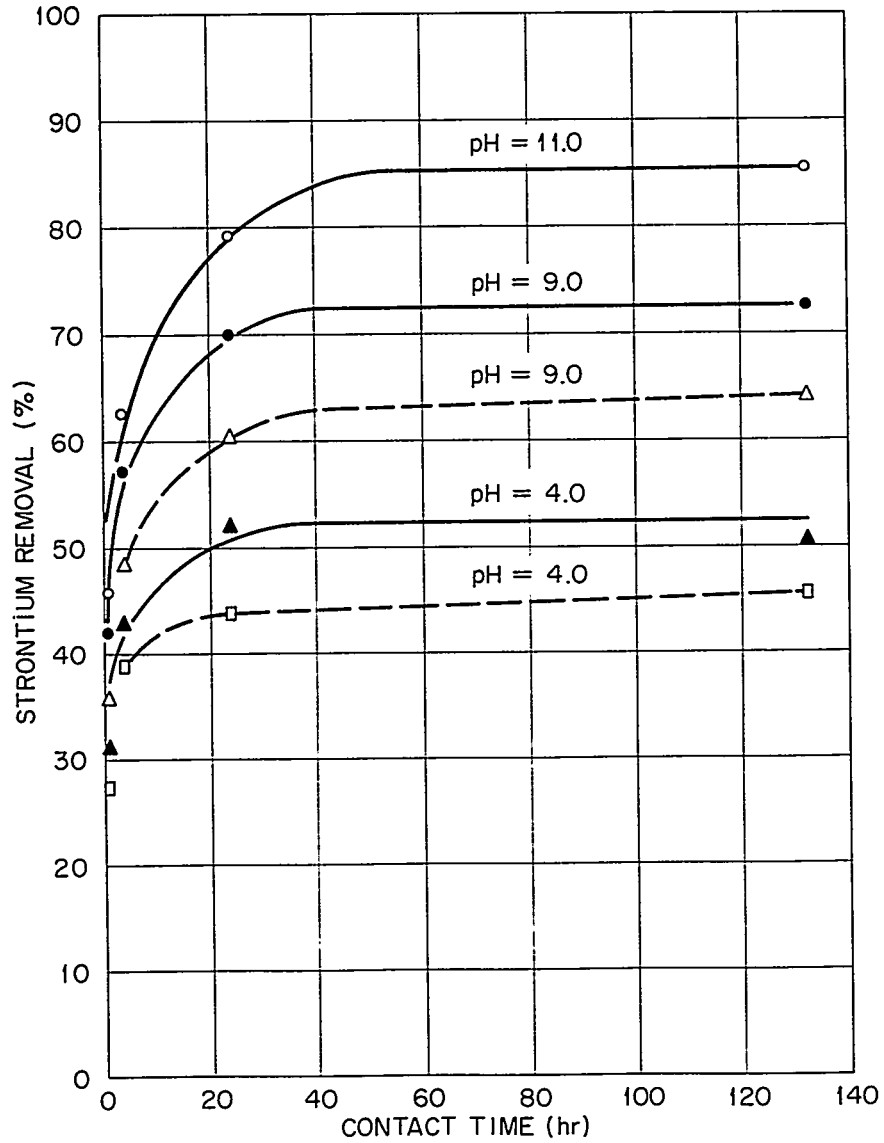


Fig. 8.2. Removal of Strontium by Na-Vermiculite Treated with NaCl-NaOH Solutions. Dashed Curves Refer to NaCl Treated Only.

Extension of cesium sorption studies to reference clay mineral systems showed that a third sorption mechanism was operative in the case of vermiculite. In the case of this mineral, high concentrations of cesium or potassium, result in a reduction of the (001) lattice spacing from ~ 14.2 Å to approximately 10 Å, causing a physical entrapment of interlayer exchangeable cations. This entrapment process may be called "interlayer fixation" to differentiate it from the "edge fixation" mechanism. Analysis of the data obtained in studies of the mechanism of "interlayer fixation" indicated that below critical concentrations of ions which induce lattice collapse, no lattice collapse occurs. Inspection of the data suggests that it is first necessary to satisfy "edge fixation" sites before any appreciable quantities of the collapse-inducing cations are available for interlayer exchange. Thus the number of the selectivity of "edge fixation" sites for various collapse-inducing cations would control the minimum concentration of the cation necessary to initiate lattice collapse and interlayer fixation. Also, the concentration of cations necessary to initiate lattice collapse is not sufficient to effect collapse of all lattices, even when the solution is continually replenished by column operation. Discussions with Tamura have led to the speculation that all interlayer spacings are not equivalent in this system, and it is suspected that interlayer charge density plays an important role in determining which interlayer spacings will be most easily collapsed.

For reasons of safety it would be an advantage to seal cesium in the "interlayer fixation" sites where the possibility of its desorption is markedly decreased. Also, from the point of view of a waste disposal operation it would be desirable to lengthen the life of a cesium-sorbing exchange column. Both objectives can be attained by adjusting ion concentrations to attain interlayer fixation rather than edge fixation. It is not practical to consider increasing cesium concentrations in waste streams due to the prohibitive costs of cesium salts. However, the same ends can be realized with increased concentrations of potassium. Potassium would collapse the vermiculite lattice and interlayer cesium would be entrapped along with it. Although the potassium would compete with cesium for interlayer exchange sites subjected to interlayer fixation, there are approximately 45 meq/100 g of these sites available compared to approximately 0.015 meq/100 g of the edge-fixation sites. The net affect is a greatly increased capacity of a column for fixation of cesium (Table 8.3).

Because collapse of all interlayer spacings does not occur at the minimum concentration for initiating lattice collapse and because increases in potassium concentration increase competition for exchange sites with cesium, it would be necessary to optimize the potassium/sodium ratio for best cesium removal. It appears that optimum conditions would be to operate at the minimum $(K^+)/ (Na^+)$ until the easily collapsed lattices are all in the collapsed state. This would be evident from an increase of cesium in the effluent. Gradual increases of the $(K^+)/ (Na^+)$ would result in more and more lattice collapse and increased cesium sorption, until finally a state would be reached where all possible collapse had been accomplished. Beyond this point, increases in potassium concentration would merely interfere with cesium sorption, though previous studies have shown that very little of the fixed cesium would be desorbed by the increased amounts of potassium.

Table 8.3 Effect of Potassium Ion Concentration on Sorption of Cesium by Zonolite*
(BO-3) from 0.5 M NaNO₃ Containing the Mass Equivalent of 2 µc Cs-137/ml

Potassium Concentration (M)	Cesium K _d (ml/g)	Observation
10 ⁻⁴	15	Apparently no collapse
10 ⁻³	9.5	Apparently no collapse
10 ⁻²	925	Some indication of inter-stratification with a small amount of 10 A spacing
10 ⁻¹	44	Nearly perfect 10 A spacing

*Hydrobiotite obtained commercially from Zonolite Company, Traveler's Rest, S. C.

9.0 WHITE OAK CREEK BASIN STUDY*

9.1 Sources of Contamination in White Oak Creek (K. E. Cowser and T. Lomenick)

9.1.1 Seeps from Burial Grounds 4 and 5

Activity has been detected in seeps, streams, and 8 of the 16 wells in the recently abandoned Burial Ground 4 (25,26) (see Fig. 9.1). The amount of activity observed in the wells varied with the sampling date. By comparing gross counts with water-level elevations in the wells at the time the samples were taken, some relations are noted. In the case of Wells 194 and 185, the rise in water-table elevation during the wet season is accompanied by a particularly noticeable increase in gross counts (Fig. 9.2). Prior to the increase in water levels the wells contained only trace amounts of activity. For Wells 182, 191, 196, and 197 the trend seems to be toward a lower concentration of activity as the water table rises. The activity in Wells 186 and 195 was so erratic that no relation with ground-water level elevation is apparent.

*This project, entitled "Environmental Radiation Studies: Evaluation of Fission Product Distribution and Movement in White Oak Creek Drainage Basin" (AEC Activity Number 06 05 01) is supported by the U. S. Atomic Energy Commission's Division of Biology and Medicine. All other projects covered in this Bimonthly Progress Report are supported by the Division of Reactor Development (AEC Activity No. 04040502).

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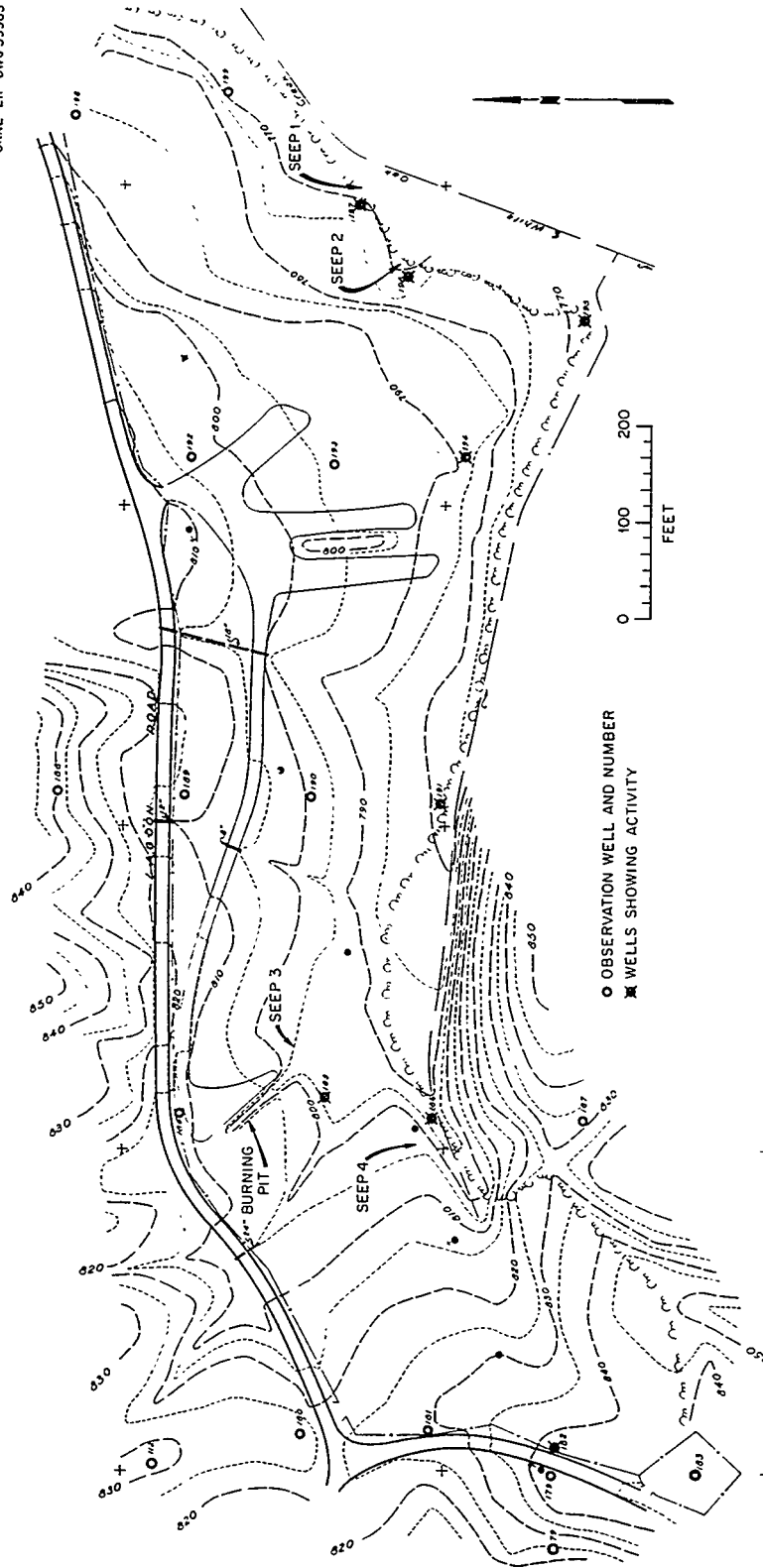


Fig. 9.1. Wells and Seeps Showing Activity at Burial Ground 4.

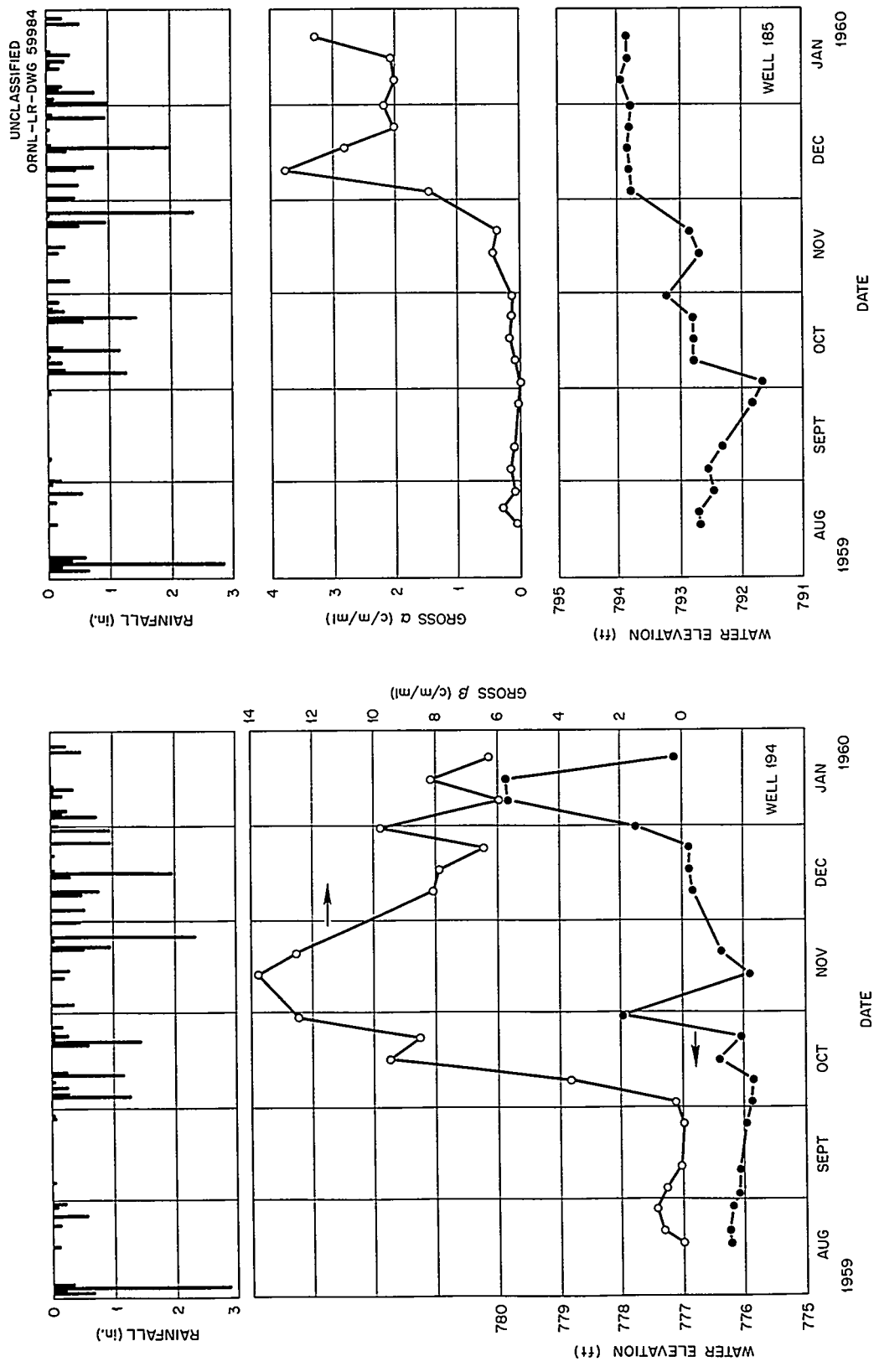


Fig. 9.2. Comparison of Gross Beta Activity and Water Level Elevations in Well 194 and Gross Alpha Activity and Water Level Elevations in Well 185.

Although there seems to be a direct relation between activity in some of the contaminated wells and ground-water-level elevations in the wells, the reasons are not clear. Perhaps the additional amount of water accompanying a rise in water level is simply diluting the waste solution, or the rise in water table may cause additional leaching of the waste, resulting in higher concentrations of radionuclides. Other conditions complicate interpretation of these data. The heterogeneous nature of the waste, the lack of detailed information on burial operations, and the lack of specific information about the waste, e.g., the type, concentration, chemical state, and amount of activity, prevent a more complete understanding of these relations.

In Table 9.1 the chemical analyses of composite well samples, as well as seep and stream samples, are compared to the analyses of uncontaminated well samples taken at Burial Ground 5 prior to its use. The relatively high concentrations of Na, Cl^- , NO_3^- , and $\text{SO}_4^{=}$ ions found in the contaminated water samples show that chemical ions are also being leached from the buried material.

Table 9.1 Chemical Analyses of Water from Auger Wells, Seep, and Stream in Burial Ground 4 and Noncontaminated Auger Wells in Burial Ground 5

	Amount (ppm)					Total Hardness as CaCO ₃
	Ca	Na	NO ₃ ⁻	Cl ⁻	SO ₄ ⁼	
Contaminated Wells in Burial Ground 4						
Wells						
182	50	92	24	74	800	749
191	30	34	20	32	71	211
194	394	58	88	674	780	1420
196	40	56	19	59	143	295
197	67	56	29	87	163	270
Seep 2	26	72	32	78	78	194
Stream	25	41	35	39	51	147
Noncontaminated Wells in Burial Ground 5*						
Composite Sample of 4 wells	68	2.1	1.2	1.3	8.7	193

* Samples at Burial Ground 5 taken prior to burial.

9.1.2 Small Tributary Draining Northwest Portion of Basin

The tributary system draining the northwest portion of the White Oak Creek Drainage Basin (1.2 sq mi) was sampled continuously and in proportion to discharge for the period Sept. 23-Oct. 28, 1960. During this time 7600 μc of Sr-89-90, 2700 μc of the rare earths (exclusive of Y-90), 530 μc of Cs-137, and 13 μc of Zr-Nb-95 were contributed to White Oak Creek. Included in this drainage area, which comprises ~20% of the total area of the White Oak Creek Drainage basin, are waste Burial Ground 3 and the extreme northwest portion of the ORNL plant site.

This contamination is the result of rainfall and surface runoff leaching and transporting soils contaminated by Laboratory fallout and general fallout (~3 curies/sq mi/year), seepage from Burial Ground 3, and as yet unknown or undefined sources.

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